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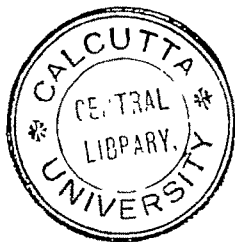
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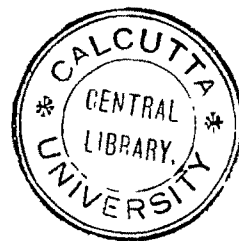
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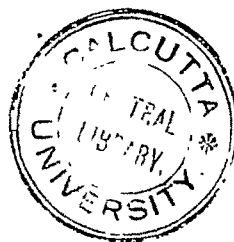
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COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS. PART X. HYDROXO-AQUO COBALTIC BISBIGUANIDINE AND ITS SALTS.

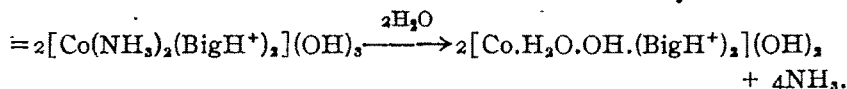
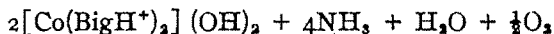
BY PRIYADARANJAN RÂY AND SAILAJA PRASAD GHOSH.

Diaminocobaltic *bis*biguanide complex has been prepared from the oxidation of cobaltous biguanide in presence of ammonia. The removal of ammonia from the latter with consequent hydrolysis in aqueous solution has led to the production of hydroxo-aquo-cobaltic *bis*biguanide complex, resembling the corresponding chromium derivative. A series of salts, *viz.* sulphate, chloride, nitrate, dithionate, sulphite and thiosulphate, have been prepared, besides the free hydrated base. The last named, on dehydration, gave rise to a diol-dicobalt-*tetrakis*biguanidine. The violet thiosulphate, on treatment with water or with an excess of sodium thiosulphate, gave a green, insoluble product which proved to be a μ -thiosulphato-*tetrakis*biguanide dithiosulphato-dicobalt. The complex hydroxo-aquo sulphate gave on dehydration a sulphato-hydroxo-cobaltic *bis*biguanide with elimination of the aquo-group from the complex by the sulphato radical.

In a previous communication of the series (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, **16**, 621) an account of the cobaltic *tris*biguanidine and its various salts, which closely resemble the corresponding chromium compounds (Rây and Saha, *ibid.*, 1937, **14**, 670), was given. Hence, the preparation of chromium *bis*biguanidine and its salts (Rây and Saha, *ibid.*, 1938, **15**, 353, 633) at once suggested the possibility of formation of similar cobalt complexes, a description of which is given in the present paper.

Chromium *tris*biguanidine salts were found to hydrolyse slowly in aqueous solution into hydroxo-aquo-*bis*biguanidine derivatives with elimination of a molecule of biguanide (Rây and Saha, *loc. cit.*). Cobaltic *tris*biguanidine compounds on the other hand are quite stable and remain perfectly unaltered in aqueous solution either on keeping for a long time or when heated. The preparation of cobaltic *bis*biguanidine compounds—the hydroxo-aquo-cobaltic *bis*biguanidine derivatives—can, however, be directly made from the cobaltous *bis*biguanidine hydrate by oxidising the latter with air in presence of strong ammonia, a red diaminocobaltic *bis*biguanide derivative being produced as an intermediate product. The latter, on further treatment with air in aqueous solution, loses ammonia giving rise to a violet liquid, which, on neutralisation with

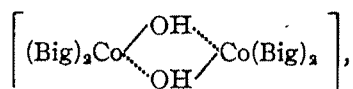
sulphuric acid and keeping in the cold, yields red-violet crystals of the sulphate.



where $\text{BigH} = \text{C}_2\text{N}_3\text{H}_7$, one molecule of biguanide.

These hydroxo-aquo-cobaltic complexes are very similar to the corresponding chromium compounds in all respects, but much more stable than the latter.

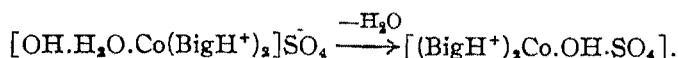
The hydroxo-aquo-cobaltic bisbiguanidinium hydroxide hydrate, $[\text{Co}(\text{BigH}^+)_2.\text{OH.H}_2\text{O}](\text{OH})_2.\text{H}_2\text{O}$, when heated to 80° , loses water even from the complex zone (total loss of water = 20.78%), giving rise to a dark brown product of the composition $\text{Co}(\text{Big})_2\text{OH}$, which can be represented by the only constitution,



(A diol-tetrakisbiguanidine dicobalt).

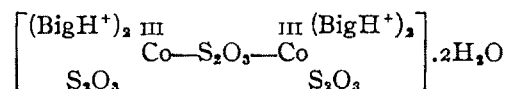
This is supported by the fact that on exposure to air the diol compound regains only 7.8% of its own weight of water without any change of its colour. An evidence in favour of the *cis*-configuration of the hydroxo-aquo-cobaltic bisbiguanide compounds is derived from this.

The violet hydroxo-aquo-sulphate, when heated to 80° , lost not only its 2.5 molecules of water of crystallisation but also the water molecule from inside the complex zone, giving rise to a brownish violet acido-hydroxo derivative—a behaviour analogous to that of the chloride of the chromium series (Rây and Saha, *loc. cit.*). No diol derivative was, however, formed in this case, because the dried product regained its violet colour and almost all its original water.

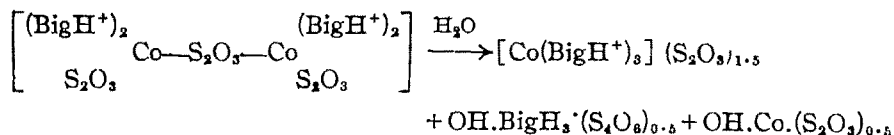


The chloride $[\text{OH.H}_2\text{O.Co}(\text{BigH}^+)_2]\text{Cl}_2.\text{H}_2\text{O}$, which crystallises with one molecule of water, loses its crystal water at 90° and more at higher temperature leading to the partial formation of a chloro-hydroxo derivative, $[\text{OH.Cl.Co}(\text{BigH}^+)_2]\text{Cl}$.

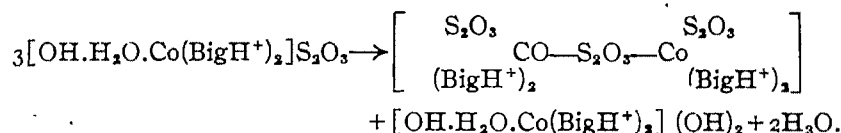
The preparation of hydroxo-aquo-cobaltic *bisbiguanidinium* thiosulphate has revealed an interesting phenomenon. By the action of a solution of sodium thiosulphate on that of the complex chloride in equivalent amount in the cold, violet crystals of the hydroxo-aquo-thiosulphate were readily precipitated. If, however, an excess of thiosulphate solution be added, or if the violet crystals be left in contact with the solution for some time, specially in the presence of a trace of dilute acetic or other acids, an almost insoluble green product of the composition, $[\text{Co}(\text{BigH}^+)_2]_2 (\text{S}_2\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$, is obtained. At 90° this loses its water molecules without any change of colour. None of the thiosulphate groups could be removed by treatment with barium chloride solution in the cold. The substance reacted neutral to litmus. On boiling with water it decomposed giving an orange solution (alkaline reaction) and a dull green residue. From the orange solution crystals of cobaltic *trisbiguanidinium* thiosulphate separated out on cooling. After filtering off the latter, the solution was found to contain biguanide and $\text{S}_4\text{O}_6^{2-}$ (tetrathionate) besides $\text{S}_2\text{O}_3^{2-}$ (thiosulphate). The dull green residue, on analysis, proved to be a basic cobaltous thiosulphate. From a consideration of all these facts the following constitution



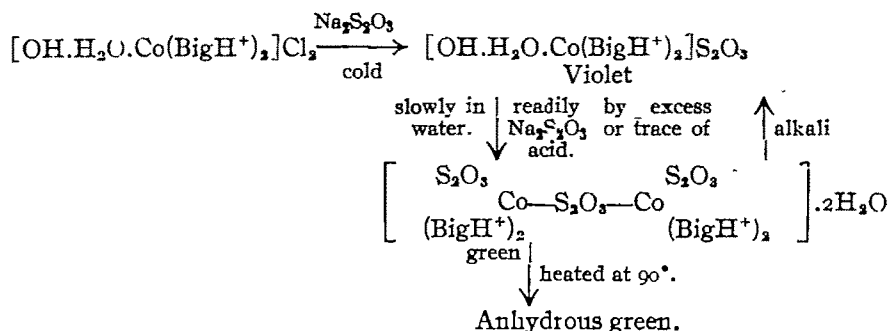
might be assigned to the above described green product, one of the thiosulphate groups acting as a bridge between the two cobalt atoms. The alternative formula, $[\text{S}_2\text{O}_3 \cdot \text{OH}_2 \cdot \text{Co}(\text{BigH}^+)_2]_2 \cdot \text{S}_2\text{O}_3$ is barred by the fact that the water molecule is lost below 90° and hence is unlikely to be present inside the complex zone. Moreover, no ionisable thiosulphate radical could be detected by treatment with barium chloride solution, though silver nitrate and lead acetate removed all the thiosulphate from the substance. A third possible structure, $[\text{S}_2\text{O}_3 \cdot \text{Co}(\text{BigH}^+)_2]_2 \cdot \text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, is also untenable for the reasons already stated. Besides, it is a well established fact that the thiosulphate radical usually occupies only one co-ordination position. The decomposition of the green product by boiling with water is rather complicated and can be represented more or less as follows.



It was observed that when the violet hydroxo-aquo-thiosulphate changes to the green product in contact with water, the latter turns strongly alkaline. This is obviously due to the formation of some free hydroxo-aquo base as represented in the following scheme.



The formation of the green product from the violet hydroxo-aquo salt, as already stated, is accelerated by the addition of a trace of acetic acid. On the other hand, it has been found that the reverse change occurs by the addition of dilute alkali to the green substance. The behaviour of the violet and the green product and their mutual conversion are summarised below.



Besides the compounds described above, nitrate, sulphate and dithionate of the complex cobaltic bisbiguanide have been prepared.

EXPERIMENTAL.

Diaminocobaltic bisBiguanidinium Sulphate.—Cobaltous bisbiguanidine, prepared by the action of strongly alkaline (with NaOH) biguanide sulphate solution in calculated quantity upon a solution of cobalt chloride, was washed free of alkali by decantation as rapidly as possible to avoid oxidation by air. The product was filtered, treated with concentrated ammonia and the mixture was oxidised by passing a brisk current of air through it for several hours, fresh ammonia being added from time to time. The silky yellow crystalline biguanidine gradually dissolved to form a red

solution leaving a little brownish black residue. This was filtered off. The filtrate often deposited red crystals on cooling. The liquid was then neutralised with dilute sulphuric acid and kept in the cold for a day or two, when red crystals of diamino-cobaltic bisbiguanidinium sulphate separated out from the solution. These were purified by recrystallisation from dilute ammonia. The purified product was first washed with cold water containing a little ammonia, then with alcohol and afterwards dried in air. The substance dissolves in cold water forming a red solution which, on slight warming, readily turns violet due to the formation of hydroxo-aquo-cobaltic bisbiguanidinium sulphate by hydrolysis. {Found: N, 30.60; Co, 10.84; SO_4 , 26.46. $[(\text{NH}_3)_2\text{Co}(\text{BigH}^+)_2]_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ requires N, 30.71; Co, 10.78; SO_4 , 26.34 per cent}.

Hydroxo-aquo-cobaltic bisBiguanidinium Sulphate.—The red solution, formed from cobaltous biguanidine and ammonia during the preparation of the previous compound, on further treatment with air current for a long time, gradually turned violet with separation of some brownish black precipitate. When the colour of the liquid became quite deep violet, or when violet crystals appeared on the walls of the vessel, it was filtered. The filtrate was then neutralised with dilute H_2SO_4 and kept in the cold for crystallisation when beautiful, needle-shaped, violet crystals separated in quantities on the walls of the basin in a day or two. These were admixed with a small amount of orange-coloured crystals of cobaltic trisbiguanidium sulphate. These latter were removed by digesting the product several times with hot water in a mortar. The purified violet crystals were then filtered, washed first with cold water, then with alcohol and finally dried over CaCl_2 .

The substance forms long rectangular violet prisms, sparingly soluble in hot water. It is decomposed by mineral acids. {Found: N, 31.80; Co, 13.53; SO_4 , 22.14. $[\text{OH} \cdot \text{H}_2\text{O} \text{Co}(\text{BigH}^+)_2] \text{SO}_4 \cdot 2.5\text{H}_2\text{O}$ requires N, 32.03; Co, 13.50; SO_4 , 21.97 per cent}.

When heated to 80° , the substance lost 14.4% of water ($3.5\text{H}_2\text{O}$) and corresponded to the composition, $[\text{OH} \cdot \text{SO}_4 \cdot \text{Co}(\text{BigH}^+)_2]$, a sulphato-hydroxo-bisbiguanidinium cobalt. The colour changed to brownish violet. On exposure to air at the ordinary temperature the product regained its original violet colour with absorption of 14.2% of its own weight of water (3 mols), corresponding to a dihydrated hydroxo-aquo-cobaltic bisbiguanidinium sulphate.

Hydroxo-aquo-cobaltic bisBiguanidinium Chloride.—The complex sulphate was digested with a cold concentrated solution of the calculated quantity of barium chloride in a mortar till the decomposition was complete.

From the filtrate from barium sulphate, the complex chloride was precipitated by the addition of absolute alcohol. The crystals of the chloride were dissolved in water and purified by reprecipitation with alcohol. The substance forms violet, rectangular prisms like the sulphate. {Found: N, 35.88; Cl, 18.60; Co, 15.44. $[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{Co}(\text{BigH}^+)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ requires N, 36.36; Cl, 18.44; Co, 15.31; per cent}.

Equivalent conductivity at 26°.

| | | | | | | |
|-------------------------------|-------|--------|--------|--------|--------|--------|
| <i>v</i> (dilution in litres) | 32 | 64 | 128 | 256 | 512 | 1024 |
| λ_v ... | 93.76 | 100.96 | 107.90 | 110.41 | 114.12 | 121.16 |
| λ_∞ (mean) ... | 120.6 | | | | | |

$\lambda_\infty = \lambda_v (1 + n_1 \times n_2 \cdot 0.692 \cdot v^{-\frac{1}{2}})$, where n_1 and n_2 are the valences of the cation and the anion (cf. Walden, "Leitvermögen der Lösungen," 1925, **V**, p. 33).

The equivalent mobility of $[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{Co}(\text{BigH}^+)_2]^{++} = 120.6 - 76.54 = 44.06$, the ionic mobility of chlorine being 76.54 at 26°. The value is somewhat lower than that of the corresponding complex chromium ion, λ_{1024} for which is 136.1 mhos at 28.3° (Rây and Saha, *loc. cit.*).

At 85° the substance loses 4.2% of water, which corresponds to its water of hydration ($\text{H}_2\text{O} = 4.7\%$). Further loss occurred above 90° and the substance decomposed at 120° with loss of 8.9% of water.

The violet solution of the chloride, when heated to boiling, turns brown with slight decomposition.

Hydroxo-aquo-cobaltic bisBiguanidinium Hydroxide and Diol-tetrakisBiguanidine Dicobalt.—The dark violet, needle shaped crystals of the base were precipitated by the addition of cold caustic soda solution to that of the complex chloride. These were washed first with ice-cold water, then with alcohol and finally dried in CO_2 -free air. [Found: N, 40.02; Co, 16.86. $[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{Co}(\text{BigH}^+)_2](\text{OH})_2 \cdot \text{H}_2\text{O}$ requires N, 40.20; Co, 16.95 per cent}.

When heated to 80° the substance loses 20.78% of water forming a dark brownish violet product—the diol-*tetrakisbiguanidine dicobalt* (Calc. H_2O , 20.70%). On exposure to air at the room temperature the diol compound absorbed 7.8% of its own weight of water forming a partial hydroxide.

The aqueous solution of the base, when heated to boiling, decomposes with separation of a brown precipitate.

Hydroxo-aquo-cobaltic bisbiguanidinium nitrate was prepared by neutralising an aqueous solution of the above described base with dilute nitric acid and precipitating the complex nitrate from the solution by alcohol.

The violet crystals were washed first with ice-cold water, then with alcohol and afterwards dried in air. {Found: Co, 14.10; NO₃, 29.85. [OH.H₂O.Co(BigH⁺)₂](NO₃)₂ requires Co, 14.03; NO₃, 29.52 per cent}.

Hydroxo-aquo-cobaltic bisBiguanidinium Sulphite.—Blue crystals of the sulphite were precipitated by the addition of a cold, freshly prepared solution (neutral) of sodium sulphite to the cold mother-liquor left after the separation of the complex sulphate. The crystals were washed with cold water and alcohol. They were then dried over CaCl₂. {Found: Co, 15.70; SO₃, 21.85. [OH.H₂O.Co(BigH⁺)₂]SO₃ requires Co, 15.68; SO₃, 21.28 per cent}.

Hydroxo-aquo-cobaltic bisBiguanidinium Dithionate.—Deep violet crystals of the dithionate were precipitated by the addition of a strong solution of sodium dithionate to that of the complex chloride. These were purified by recrystallisation from warm water. {Found: Co, 12.48; S₂O₆, 33.95. [HO.H₂O.Co(BigH⁺)₂]S₂O₆.H₂O requires Co, 12.44; S₂O₆, 33.76 per cent}.

When heated to 105° it lost its water of hydration (Found: H₂O, 3.8%. Calc. H₂O, 3.79 per cent). No more loss occurred when the substance was further heated up to 130°.

Hydroxo-aquo-cobaltic bisBiguanidinium Thiosulphate.—Needle-shaped, violet crystals of the thiosulphate were precipitated by mixing solutions of the equivalent amounts of the complex chloride and sodium thiosulphate in the cold. The crystals were immediately filtered, washed first with ice-cold water and then with alcohol. These were dried in air. {Found: Co, 13.75; S₂O₃, 26.42. [OH.H₂O.Co(BigH⁺)₂]S₂O₃.H₂O requires Co, 13.81; S₂O₃, 26.30 per cent}. The substance turns green on shaking with water and the supernatant solution becomes violet-red with alkaline reaction.

Thiosulphato-tetrakisbiguanidinium Dithiosulphato-dicobalt.—When, however, a solution of an excess of sodium thiosulphate was added to that of the complex chloride, the violet thiosulphate, first formed, changed immediately into a bright green insoluble product. The same substance was also obtained by the addition of an excess of sodium thiosulphate to the mother-liquor after the separation of the complex sulphate. The pure violet thiosulphate also changes into the green product on shaking with water and more readily by the addition of a trace of acid. {Found: N, 31.48;

Co, 13.14; S₂O₃, 37.80.
$$\left[\begin{array}{ccc} \text{S}_2\text{O}_3 & & \text{S}_2\text{O}_3 \\ & \text{Co—S}_2\text{O}_3\text{—Co} & \\ (\text{BigH}^+)_2 & & (\text{BigH}^+)_2 \end{array} \right] \cdot 2\text{H}_2\text{O}$$
 requires N, 31.32; Co, 13.18; S₂O₃, 37.58 per cent}.

At 90° it lost 4.03 per cent of water. The dried substance gave (Co, 13.80. Calc. : Co, 13.74 ; H₂O, 4.03 per cent). There was no change of colour on dehydration.

The substance is almost insoluble in water. When digested in the cold with barium chloride solution there was no reaction. On boiling with water it decomposed as described before (*vide supra*). When treated with a solution of silver nitrate or lead nitrate all the thiosulphate were removed with formation of a cobaltic trisbiguanide salt in solution, which reacted acid. In the case of silver nitrate, black silver sulphide was formed from the decomposition of silver thiosulphate first produced.

By the action of sodium nitrite solution on a solution of the complex chloride a moderately soluble, brick-red precipitate was obtained. It was alkaline in reaction. An orange-yellow precipitate, neutral in character, was obtained by adding a solution of sodium nitrite to the mother-liquor left after the separation of the complex sulphate. By digesting the complex sulphate with a solution of barium nitrite a third compound, orange-red in colour and soluble in hot water, was isolated. All these substances were found to contain NO₂ groups, but none of them could be made sufficiently pure to give definite composition.

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COMPLEX FORMATION IN AQUEOUS MERCURIC CHLORIDE AND POTASSIUM IODIDE BY CONDUCTIVITY, VISCOSITY AND REFRACTIVITY MEASUREMENTS.

BY DUSHYANT NARASINGASA SOLANKI AND BHASKAR GOVIND JOSHI

Complex formation in aqueous mercuric chloride and potassium iodide has been studied by the conductivity, viscosity, and refractivity measurements. The occurrence of breaks (maxima or minima) in specific conductivity, viscosity, and refractivity composition curves has been attributed to the existence of molecular complexes of mercuric chloride and potassium iodide.

Jaques ("Complex Ions in Aqueous Solutions," Longmans, Green & Co., London, 1914, p. 48) has given an exhaustive review of the earlier work on mercuric chloride-alkali chloride complexes in aqueous system. The complexes of the type M_2HgX_4 , $MHgX_3$, in aqueous and non-aqueous solutions seem to have been reported by many investigators on freezing point, E.M.F., solubility and other independent grounds.* The importance of the reaction between KI and $HgCl_2$ in analytical chemistry was pointed out by Koninck and Lebrun (*Chem. Zentr.*, 1902, II, 72), Kolthoff (*Pharm. Weekblad*, 1920, 57, 836) and others. Complexes of $HgCl_2$ or HgI_2 with KI in alcohol or acetone solutions have been studied by conductivity measurements (cf. Pernot, *Compt. rend.*, 1927, 188, 950; *Ann. Chim.*, 1931, x, 15, 5; Gallais, *Compt. rend.*, 1932, 195, 875). Foote and Martin (*Amer. Chem. J.*, 1909, 41, 451) measured the conductivities of alkali chlorides in fused $HgCl_2$ at 282° ; abnormal rise in conductivity was attributed to complex formation. Job (*Compt. rend.*, 1925, 180, 1932), Shibata and Ionone (*Japan J. Chem.*, 1926, 2, 109), and Samuel, Zaman and Zubairy (*Indian J. Phys.*, 1935, 9, 491) studied the formation of complex mercury salts by spectroscopic means. The present work, being an outcome of interesting results of Sharma and Kadhe in these laboratories, is intended to study complex formation in aqueous $HgCl_2$ and KI by conductivity, viscosity and refractivity measurements.

* Cf. LeBlanc and Noyes, *Z. physikal. Chem.*, 1890, 6, 401; Clayton, *Chem. News*, 1894, 70, 1027; Pawloff, *J. Russ. Phys. Chem. Soc.*, 1900, 32, 732; Dobroserdoff, *ibid.*, 1901, 33, 392; Sherill, *Z. physikal. Chem.*, 1903, 43, 705; Sand and Breest, *ibid.*, 1907, 69, 424; Dawson, *J. Chem. Soc.*, 1909, 98, 870; Bonrion and Rouyer, *Compt. rend.*, 1924, 178, 86, 1171; Vajnik and Uberoy, *J. Amer. Chem. Soc.*, 1924, 46, 802.

E X P E R I M E N T A L.

Merck's guaranteed extra pure mercuric chloride and potassium iodide were used. Conductivity measurements of aqueous KI ($M/20$ and $M/50$) in presence of varying proportions of $HgCl_2$ were made at 15° and 30° , observing the usual precautions (*cf.* earlier communications by Joshi and Solanki, *J. Indian Chem. Soc.*, 1937, **14**, 323, 1940, **17**, 627). The maximum concentration of $HgCl_2$ was such as to avoid the actual precipitation of HgI_2 in the solution. The cell constant determined by using freshly prepared $N/50$ -KCl solution at $25^\circ \pm 0.1^\circ$ was 0.3776. The same cell constant was used for calculating the conductivity at 15° and 30° , its variation with temperature, especially for 5° - 10° differences, being negligible.

The viscosity determinations of the mixed solutions of KI and $HgCl_2$ were also made at 15° and 30° by adopting Ostwald's method. Extreme precautions were taken specially in cleaning the viscometer and in maintaining the temperature control within 0.05° . The densities corresponding to these solutions were determined at the above temperatures.

The refractive index for the sodium line was determined for each of the above mixtures by means of Pulfrich refractometer at 15° and 30° with the usual precautions.

The strength of the mixture in terms of its components, potassium iodide and mercuric chloride, is recorded in column 1 in Tables I—IV; the concentrations of the components are expressed for the system *after mixing*. Column 2 gives the resistance in ohms for the mixed solutions. In column 3 are given the specific conductivities in mhos for the mixtures; in column 4 are given the specific conductivities for the corresponding concentrations of mercuric chloride present in the mixture as shown in column 1. Column 5 gives the percentage departure of the specific conductivity of the mixture (column 3) from that calculated by applying the additive rule. Columns 6 and 7 give respectively the viscosities and densities of the mixtures. The refractivity data for these mixtures are shown in column 8 and 9; column 8 gives the angle of emergence after correction for zero error and column 9 gives the refractive index for sodium line. All these results for the mixtures are shown graphically in Figs. 1 to 4. The quantities, *viz.*, the specific conductivity, percentage departure of the specific conductivity from that obtained by the additive rule, viscosity, density and refractive index are plotted against the concentration of mercuric chloride present in the system by appropriate selection of scale units in the same figure to economise space (Figs. 1 to 4).

TABLE I.

Temperature = $30 \pm 0.05^\circ$. Mixture of M/20-KI and HgCl₂. Sp. conductivity of water = 1.37×10^{-6} mhos.

| Comp. of mixture after mixing | R of mixture in ohms. | Sp. condy. of mixture in mhos. | % Departure of the sp. condy. of mixture from additive rule | Viscosity of mixture in absolute units. | Density of the mixture in g / c c. | Angle of emergence corrected for zero error. | Refractive index of mixture. n_D . |
|-----------------------------------|-----------------------|--------------------------------|---|---|------------------------------------|--|--------------------------------------|
| M/20 KI only | 51.35 | 0.0073516 | ... | 0.0081594 | 1.0097 | 67° 13' | 1.3330704 |
| M/20 KI + M/400 HgCl ₂ | 52.80 | 0.0071506 | 3.12 | 0.0080996 | 1.0104 | 67° 10' | 1.3333044 |
| M/20 KI + 2M/400 " | 53.65 | 0.0070356 | 4.75 | 0.0081190 | 1.0110 | 67° 12' | 1.3331484 |
| M/20 KI + 3M/400 " | 54.35 | 0.0069456 | 6.06 | 0.0080790 | 1.0115 | 67° 10' | 1.3333044 |
| M/20 KI + 4M/400 " | 54.90 | 0.0068756 | 7.08 | 0.0080977 | 1.0122 | 67° 9' | 1.3333824 |
| M/20 KI + 7M/600 " | 55.40 | 0.0068146 | 7.98 | 0.0080981 | 1.0125 | 67° 9' | 1.3333824 |

TABLE II.

Temperature = $15 \pm 0.05^\circ$. Mixture of M/20-KI and HgCl₂. Sp. conductivity of water = 1.09×10^{-6} mhos.

| Comp. of mixture after mixing | R of mixture in ohms | Sp. condy. of mixture in mhos. | % Departure of the sp. condy. of mixture from additive rule | Viscosity of mixture in absolute units. | Density of mixture in g / c c. | Angle of emergence corrected for zero error. | Refractive index of the mixture. n_D . |
|-----------------------------------|----------------------|--------------------------------|---|---|--------------------------------|--|--|
| M/20 KI only | 69.5 | 0.005432 | | 0.011588 | 1.00332 | 66° 55' | 1.3344278 |
| M/20 KI + M/400 HgCl ₂ | 70.4 | 0.005362 | 1.56 | 0.011553 | 1.00357 | 66° 53' | 1.3345858 |
| M/20 KI + 2M/400 " | 71.3 | 0.005291 | 2.88 | 0.011565 | 1.00384 | 66° 53' | 1.3345858 |
| M/20 KI + 3M/400 " | 73.1 | 0.005164 | 5.31 | 0.011642 | 1.00424 | 66° 52' | 1.3346648 |
| M/20 KI + 4M/400 " | 74.45 | 0.005070 | 7.10 | 0.011610 | 1.00469 | 66° 51' | 1.3347438 |
| M/20 KI + 7M/600 " | 75.35 | 0.005009 | 8.27 | | | 66° 51' | 1.3347438 |

TABLE III.

Temperature = $30 \pm 0.05^\circ$. Mixture of M/50-KI and HgCl_2 . Sp. conductivity of water = 1.37×10^{-6} mhos.

| Comp. of mixture after mixing. | R of mixture in ohms. | Sp. condy. of mixture in mhos. | % Departure of sp. condy. of mixture from additive rule. | Viscosity of mixture in absolute units. | Density of mixture in g./c.c. | Angle of emergence corrected for zero error. | Refractive index of the mixture. | n_D . |
|----------------------------------|-----------------------|--------------------------------|--|---|-------------------------------|--|----------------------------------|---------|
| M/50 KI only | 126.5 | 0.002984 | | 0.0080429 | 1.00361 | $67^\circ 22'$ | 1.3323704 | |
| M/50 KI + M/1000 HgCl_2 | 128.2 | 0.002944 | 0.00002253 | 2.08 | 0.0080263 | $67^\circ 20'$ | 1.3325244 | |
| M/50 KI + 2M/1000 " | 129.5 | 0.002915 | 0.00002802 | 3.22 | 0.0080357 | $67^\circ 21'$ | 1.3324474 | |
| M/50 KI + 3M/1000 " | 130.0 | 0.002904 | 0.00003175 | 3.71 | 0.0080024 | $67^\circ 20'$ | 1.3325344 | |
| M/50 KI + 4M/1000 " | 131.6 | 0.002868 | 0.00003686 | 5.06 | 0.0080166 | $69^\circ 19'$ | 1.3326024 | |
| M/50 KI + 9M/1000 " | 134.3 | 0.002810 | 0.00003907 | 7.05 | 0.0080178 | $67^\circ 19'$ | 1.3326024 | |

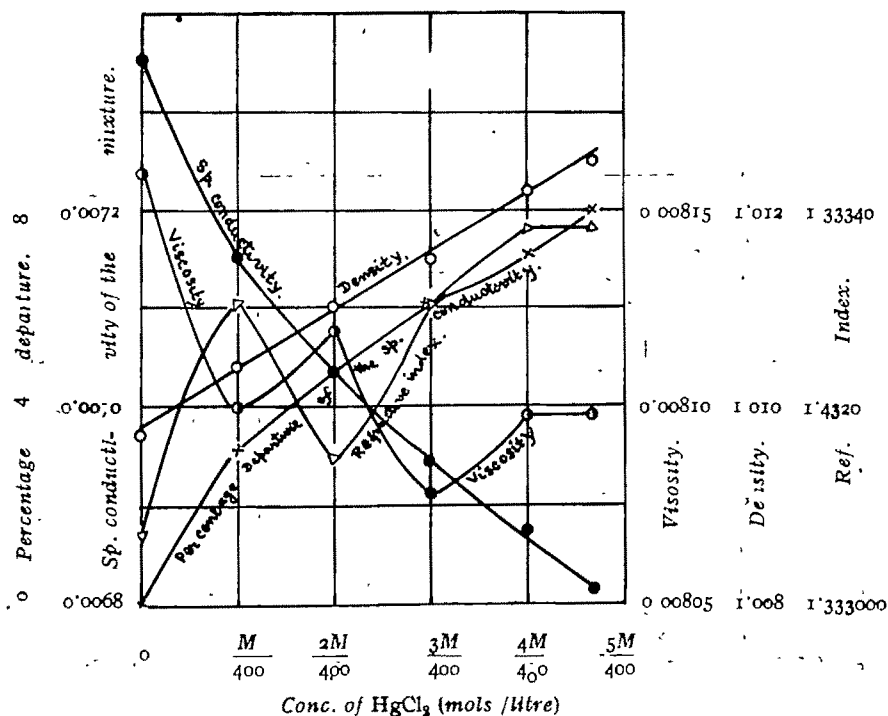
TABLE IV.

Temperature = $15 \pm 0.05^\circ$. Mixture of M/50-KI and HgCl_2 . Sp. conductivity of water = 1.09×10^{-6} mhos.

| Comp. of mixture after mixing | R of mixture in ohms. | Sp. condy. of mixture in mhos. | % Departure of the sp. condy. of mixture from additive rule. | Viscosity of mixture in absolute units. | Density of mixture in g./c.c. | Angle of emergence corrected for zero error. | Refractive index of the mixture. | n_D . |
|----------------------------------|-----------------------|--------------------------------|--|---|-------------------------------|--|----------------------------------|---------|
| M/50 KI only | 168.7 | 0.002238 | | 0.011621 | 1.00164 | $67^\circ 4'$ | 1.3337208 | |
| M/50 KI + M/1000 HgCl_2 | 171.4 | 0.002202 | 0.00001104 | 2.09 | 0.011618 | $67^\circ 2'$ | 1.3338768 | |
| M/50 KI + 2M/1000 " | 174.7 | 0.002161 | 0.00001402 | 4.64 | 0.011620 | $67^\circ 2'$ | 1.3338768 | |
| M/50 KI + 3M/1000 " | 175.5 | 0.002151 | 0.00001617 | 4.58 | 0.011643 | $67^\circ 1'$ | 1.3339548 | |
| M/50 KI + 4M/1000 " | 177.7 | 0.002123 | 0.00001859 | 5.92 | 0.011626 | $67^\circ 0'$ | 1.3340328 | |
| M/50 KI + 9M/1000 " | 180.2 | 0.002094 | 0.00002027 | 7.27 | 0.0 | $67^\circ 0'$ | 1.3340328 | |

Cell constant in all cases was 0.3776.

FIG. 1.
Temp. = 30°.

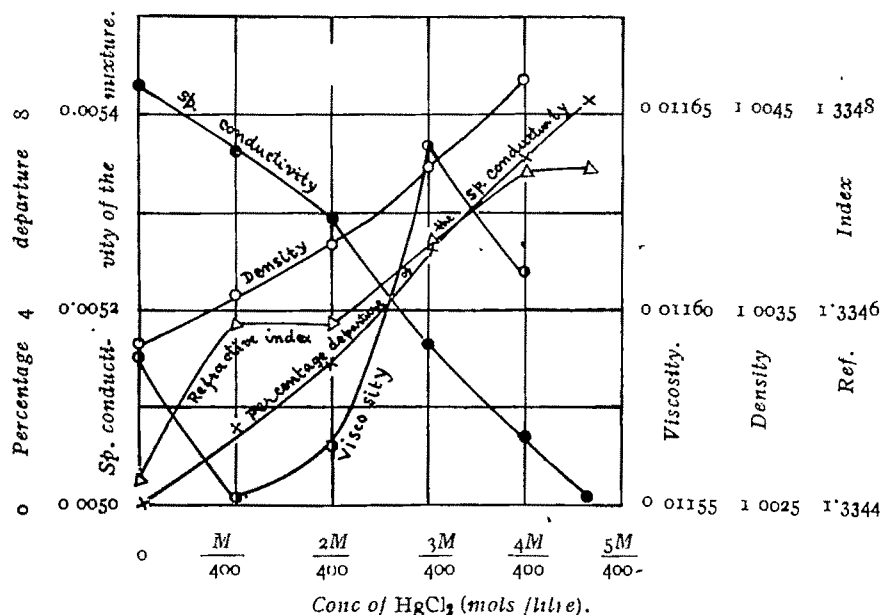


DISCUSSION.

Data shown under column 4 in Tables I-IV indicate that HgCl_2 behaves as an extremely weak electrolyte, almost a non-electrolyte as is obvious from the exceedingly low order of the specific conductivities in agreement with the results previously published (cf. Joshi and Solanki, *loc. cit.*). Results in column 3 show that with the addition of HgCl_2 , the specific conductivity of the resulting mixture of $\text{KI}(M/20$ and $M/50)$ and HgCl_2 gets diminished considerably; the diminution produced increased with increased concentration of HgCl_2 . In other words, the specific conductivities of the resulting mixtures show considerable departures (results in column 5) from those calculated by applying the additive law for the corresponding mixtures, *viz.*, the specific conductivity of the mixture equals the sum of the specific conductivities of the two components, each determined separately. For mixtures of certain salts, such as NaCl and KCl , for which no complex formation is anticipated, the deviations from additive behaviour are less than the experimental error in conductivity (cf. Sandonini, *Gazetta*, 1916, ii, 46, 205; also Jones and Oata, *Amer. Chem. J.*, 1899, 22, 5) and

refractivity measurements (cf. Eberhard, Rimbach and Wintgen, *Z. physikal. Chem.*, 1910, 74, 230). Results for the conductivity of aqueous benzoic

FIG. 2.
Temp. = 15°.



acid (cf. earlier communication from these laboratories, Joshi and Solanki, *loc. cit.*) in the presence of LiCl , NaCl , KCl , RbCl , etc., show that additive law holds for the mixture. The observed diminution in conductivity and correspondingly the departure of KI and HgCl_2 might, therefore, be attributed to complex formation. The molecular complexes of HgCl_2 and KI have been shown to exist, independently by several observers: Gallais (*loc. cit.*) by conductivity measurements, Shibata and Ionone (*loc. cit.*) and Job (*loc. cit.*) by spectroscopic methods, Bourion and Rouyer (*loc. cit.*) ebullioscopically, Yajnik and Uberoy (*loc. cit.*) by viscosity measurements and also by refractivity measurements. The specific conductivity and its percentage departure graphs in Figs. 1-4 and also viscosity and refractive index graphs in Figs. 1-3 show remarkable similarity, i.e., while the viscosity increases, refractive index decreases roughly to the same extent until in the former case a maximum and in the latter case a minimum are obtained. The occurrence of this discontinuity (except in the case of density), i.e., the minima in specific conductivity-, and in refractivity-, and

maxima in viscosity-composition curves can, therefore, be taken as indicative of complex formation and the composition of the complex formed being

FIG. 3.
Temp. = 30°

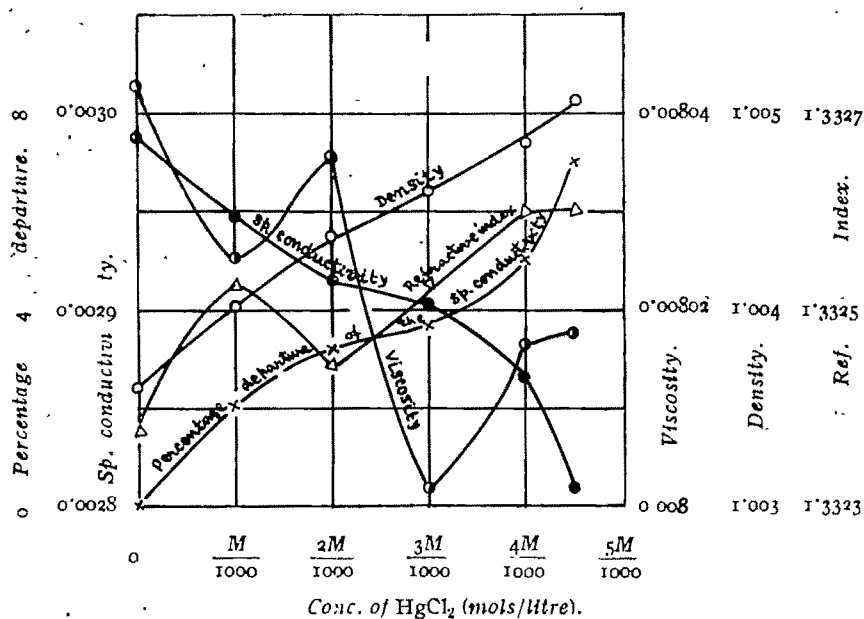
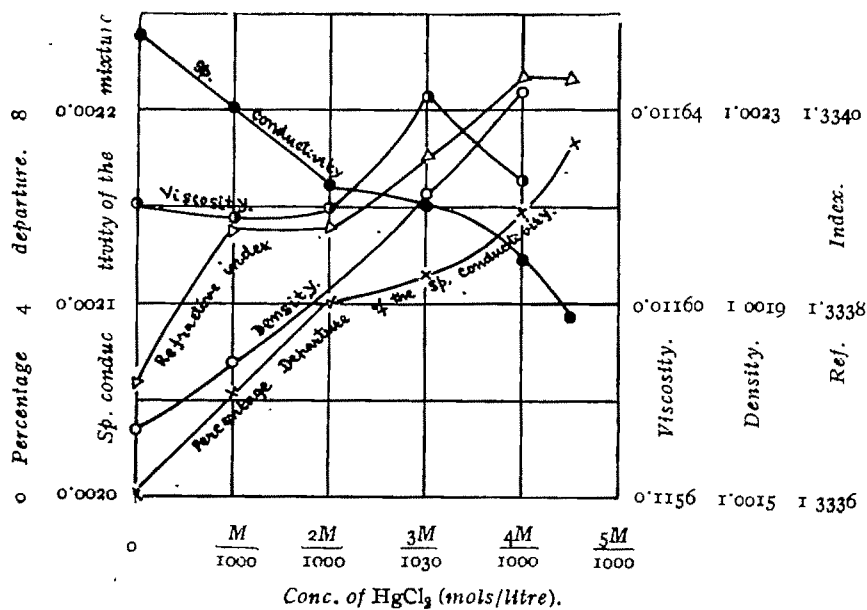


FIG. 4.
Temp. = 15°



noted from the composition corresponding to the position of minima or maxima in the respective curves (*cf.* Figs. 1-4). All the measurements lead probably to the existence of a complex of KI and HgCl_2 in the molecular proportion, 10 KI, HgCl_2 . Viscosity measurements indicated the existence of another complex 20 KI, 3HgCl_2 . Our data also show an indication of another break in the respective curves corresponding to a point in the vicinity of maximum concentration of HgCl_2 tried, roughly corresponding to a formula, 4-5 KI, HgCl_2 . The breaks in the respective curves are sharp and well defined, especially in concentrated solutions and at a low temperature thus showing that the complexes formed in the aqueous system dissociate at high temperature and dilution.

The authors express their indebtedness to Dr. S. S. Joshi, for suggesting the problem and giving valuable help and criticism during the course of the investigation.

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THE ELECTROCHEMICAL PROPERTIES OF SILICIC ACID SOLS. PART III. VARIATIONS IN THE p_H , SPECIFIC CONDUCTIVITY AND TOTAL ACIDITY OF SILICIC ACID SOLS WITH DILUTION AND WITH TEMPERATURE.*

BY B. CHATTERJEE AND A. SEN.

The free and total acidities of silicic acid sols change linearly with concentration and the degree of dissociation remains practically constant. The variation of conductivity with dilution shows departures from a linear relation. The values of the hydrogen ion concentration of the sol and its dilutions calculated from the p_H and the specific conductivity show fair agreement. The free and total acids of silicic acid sols as also their degree of dissociation do not materially change with temperature between 1° and 50°. The specific conductivity increases linearly with temperature. The temperature coefficient at 18° is about 2%.

The potentiometric titration curves of silicic acid sols with concentrated alkalis resemble those of a weak monobasic acid in true solution (Chatterjee, *J. Indian Chem. Soc.*, 1939, **16**, 589.) On the gradual addition of alkali the p_H rapidly rises to about 9.5, then at a slower rate and the curve finally shows an inflexion point (second inflexion point) between p_H 11.0 and 11.7 corresponding to the formation of NaHSiO_3 . The first dissociation constant of silicic acid has been obtained from the values of S , the concentration of dissolved silica and the following relation

$$K_1 S = [H^+] \{ [H^+] + [B^+] - [OH^-] \},$$

where K_1 is the first dissociation constant of silicic acid; B^+ , the concentration of Na^+ . K_1 has a mean value of 5.2×10^{-10} . On closer examination, however, the resemblance with a weak acid in true solution appears to be superficial. The buffer capacity ($\Delta B / \Delta p_H$) of the sol is considerably greater than that of a dissolved acid having the same dissociation constant and total acidity as the sol. Titration curves with dilute solution (0.01N) of NaOH , Ba(OH)_2 and Ca(OH)_2 show an inflexion point in the acid region between p_H 4.5 and 5.6. The range of p_H in which the inflexion point has been observed with several bases are with NaOH , 5.17 to 5.4; with Ba(OH)_2 , 4.80 to 5.6; and with Ca(OH)_2 ,

* The results given in this paper have been taken from the published annual reports for 1938-39 and 1939-40 on the working of a 'Scheme of Research into the Properties of Colloid Soil Constituents' financed by the Imperial Council of Agricultural Research, India.

4.5 to 5.5. The total acid at this inflexion point and the free acid calculated from the initial p_H of the sol are of the order of $10^{-4}N$; the degree of dissociation, i.e., the ratio of free to total acids has been found to lie between 0.5 to 1.0. The total acid neutralised at the first inflexion point is the same for all these bases. The slopes of the titration curves, however, show that the relative intensities with which different bases react with the sol are in the order $Ca(OH)_2 > Ba(OH)_2 > NaOH$. The amount of acid neutralised at the inflexion point in the titration curve with a dilute base, however, does not represent the total neutralisable acid of the sol. Much larger amounts of acids are set free by repeatedly leaching the sol with solutions of neutral salts (Chatterjee, *J. Indian Chem. Soc.*, 1939 **16**, 607). But the total acid thus found constitutes a very small fraction (about 0.0013) of the amount of silicon dioxide (estimated as orthosilicic acid) present, indicating that the reaction is confined to the surface. The amount of acid liberated by different chlorides are in the order: $Ba^{++} > Ca^{++} > Na^+ > Li^+$. In the present investigation the variations with (i) dilution and (ii) temperature have been studied. Experimental details and fuller references to previous work have been given in the two papers referred to above.

Change brought about on Dilution.

Rabinowitsch and Laskin (*Z. physikal. Chem.*, 1928, **104**, 390) studied the variations of free and total acids with dilution. They concluded that the degree of dissociation increased with dilution reaching the apparently improbable value of 330 per cent at a dilution of 128. They attributed this increase to the progressive hydrolysis of the acid anhydride molecule contained in the colloidal particles and their subsequent dissociation. The total amount of neutralisable hydrogen ions estimated by multiplying the total acidity of the diluted sols by the dilution greatly exceeds the total amount of neutralisable acid of the undiluted sol. In a later paper Rabinowitsch and Kargin (*Trans Faraday. Soc.*, 1935, **31**, 289), however, attributed the hydrogen ion activities of silicic acid sols measured by Rabinowitsch and Laskin (*loc. cit.*) and others to foreign electrolytes. In previous work in this laboratory (Mukherjee and co-workers, *Indian J. Agric. Sci.*, 1934, **4**, 733; Mukherjee, *Kolloid Z.*, 1934, **67**, 178) on the changes in the free and total acid of silicic acid sols with dilution, it was observed that the hydrogen ion activities of the sol varied with dilution in a manner different from that of an acid in true solution. The sols used by Mukherjee and co-workers contained appreciable amounts of hydrochloric acid and some of them also contained small but visible flocks. The titration curves were often irregular and showed several breaks simulating those of a polybasic

acid. These breaks were traced to the presence of these flocks and non-attainment of equilibrium and in later work in this laboratory (Chatterjee, *loc. cit.*) the improvements in the experimental technique have resulted in reproducible and smooth titration curves. The present investigation has been carried out with more carefully purified sols.

Variations in the p_H and Specific Conductivity on Dilution.

The variations with dilutions in the p_H , free acidity and specific conductivity of sols U and W are shown in Table I. Water having a specific conductivity of 1.1 to 1.15×10^{-6} mho at 35° has been used for diluting the sols.

TABLE I.

| System. | Colloid content g. mol. per litre. | p_H . | Specific conductivity $\times 10^6$ mho. | | | Free acidity $\times 10^4 N$ \times dilution. | Corrected sp. condy. $\times 10^6$ mho. \times dilution. |
|---------|------------------------------------|----------------------|--|----------------|------------|---|--|
| | | | sol. | ultrafiltrate. | corrected† | | |
| Sol U | 0.30 | 4.38 4.37 | 46.3 | 27.2 | 19.1 | 4.20 | 19.1 |
| " U/2 | 0.15 | 4.54 4.68 4.67 | 23.5 | 16.2 | 7.3 | 4.60 | 14.6 |
| " U/4 | 0.075 | 4.96 4.95 | 10.3 | 6.3 | 4.0 | 4.44 | 16.0 |
| " U/8 | 0.038 | 5.29 5.20 | 7.1 | 5.1 | 2.0 | 4.48 | 16.0 |
| Sol W | 0.26 | 3.87 3.85 3.86 | 76.5 | 9.5 | 67.0 | 13.8 | 67.0 |
| " W/2 | 0.13 | 4.13 | 35.9 | 5.2 | 30.7 | 14.8 | 61.4 |
| " W/4 | 0.065 | 4.52 | 16.5 | 3.0 | 13.5 | 12.0 | 54.0 |

* Specific conductivity of equilibrium water is calculated to be about 1.0×10^{-6} mho at this temperature.

† The specific conductivity of a sol minus that of its ultrafiltrate.

Considering the experimental errors and methods of calculation, it may be concluded from the data given in Table I that the concentration of neutralisable hydrogen ion obtained by multiplying the hydrogen ion concentration of the dilute sol by the number of times the sol has been diluted remains practically constant. The conductivity obtained by mul-

tipling the corrected specific conductivity with the dilution show variations somewhat greater than the experimental error.

Agreement between Activity and Conductivity Data.

The hydrogen ion concentrations have been calculated from their corrected specific conductivity (Table I) using the formula,

$$C_H = \frac{1000 \times \text{corrected specific conductivity}}{U_H + V_{\text{colloid}}}$$

where $U_H = 404$ and $V_{\text{colloid}} = 24$ at 35° , compared in Table II with those from the p_H values. The above value of V_{colloid} has been calculated from c.v. measurements which show that it has a value of 20 at 25° and temperature coefficient of 2 %.

TABLE II.

| System. | p_H . | Corrected* sp. condy. $\times 10^6$. | Free acidity $\times 10^4 N$ calculated from | |
|---------|---------|---------------------------------------|--|------------------|
| | | | p_H . | Corr. sp. condy. |
| Sol U | 4.38 | 19.1 mho | 4.20 | 4.47 |
| „ U/2 | 4.63 | 7.3 | 2.30 | 1.71 |
| „ U/4 | 4.96 | 4.0 | 1.11 | 0.93 |
| „ U/8 | 5.25 | 2.0 | 0.56 | 0.47 |
| Sol W | 3.86 | 67.0 | 13.8 | 15.7 |
| „ W/2 | 4.13 | 30.7 | 7.4 | 7.2 |
| „ W/4 | 4.52 | 13.5 | 3.0 | 3.2 |

The agreement should be considered fair in view of the experimental errors and the methods of calculation. Pauli and co-workers (*Kolloid Z.*, 1925, **36**, 325; 1926, **38**, 289; 1937, **79**, 67) obtained that the C_H calculated from specific conductivity was higher than those from the p_H . It is probable that account was not taken of the foreign electrolytes present in the sol.

Variations in the Total Acidity and Degree of Dissociation with Dilution.

The total acid† of sol W and its dilution as also of sol U obtained, by titration with NaOH, are given in Table III and the degree of dissociation

* Taken from Table I.

† Calculated at the first inflexion point in the titration curve with NaOH.

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calculated from the free acid given in Table II, have also been shown in the same table.

TABLE III.

| System | p_H . ° | Free acid $\times 10^6 N$ from p_H . | Total acid $\times 10^6 N$. | Degree of dissociation. (%) |
|--------|-----------|--|---------------------------------|--------------------------------|
| Sol U | 4.38 | 4.20 | 4.0 | 105 (completely dissociated) |
| Sol W | 3.86 | 13.8 | 17.8(4.85)** | 77.5 |
| „ W/2 | 4.13 | 7.4 | 9.6(4.93)** | 77.0 |
| „ W/4 | 4.52 | 3.0 | 4.1(5.37)** | 74.0 |

** Figures within brackets give the p_H at inflexion.

The total acidity of sol W changes almost linearly with concentration within the limits of experimental errors. The degree of dissociation about 77.5%, does not materially change on dilution. For the same ratio of dilution Rabinowitsch and Laskin (*loc. cit.*) observed a change from 80% to 90%.

A comparison of the free to total acidity shows that sol U is completely and sol W only 77.5% dissociated. This difference cannot, however, be ascribed only to the difference in the p_H of the two sols.

Assuming colloidal silicic acid to behave as a uni-36 valent electrolyte in true solution, calculations using the equation as developed by Onsager (*Physikal. Z.*, 1926, 27, 388) give a value of 0.774 for its degree of dissociation at a concentration of 17.8N. The variations with dilution in the degree of dissociation of such an electrolyte have been calculated and shown in Table IV.

$$\Lambda_0 - \Lambda = \frac{29.0(Z_+ + Z_-)}{(DT)^{0.5}\eta} + \frac{0.986 \times 10^6}{(DT)^{1.5}} W \Lambda_0 \sqrt{2\mu} \quad \dots (i)$$

where

$$W = Z_+ Z_- \frac{2q}{\sqrt{1+q}}$$

and

$$q = \frac{Z_+ Z_- (U_1 + U_2)}{(Z_+ + Z_-)(Z_- U_1 + Z_+ U_2)}$$

TABLE IV.

| | | | | |
|----------------------|-----|----------|----------|----------|
| Conc. (N) | ... | 0.000178 | 0.000089 | 0.000045 |
| Degree of dissn. (%) | ... | 77.4 | 83.9 | 89.9 |



The degree of dissociation of the hypothetical uni-36 valent electrolyte increases regularly with dilution, whereas that of sol W (Table II) remains practically constant. The variations in the degree of dissociation of colloidal silica are thus not in accordance with Onsager's theory.

*Changes with Temperature.**

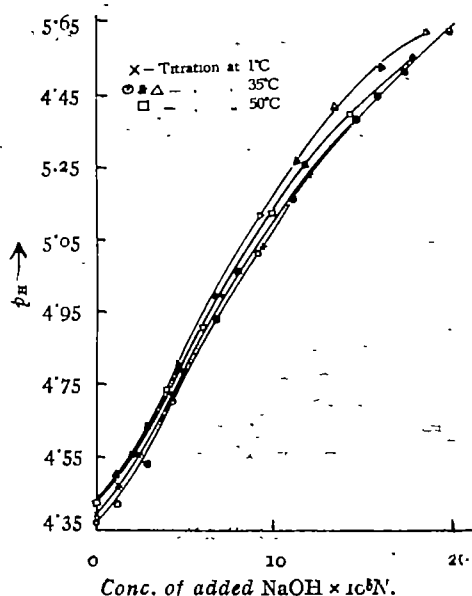
The free and total acids of three silicic acid sols T, U and W and the specific conductivity of sols T and W at several temperatures are shown in Table V.

TABLE V.

| Sol. | Specific conductivity $\times 10^6$ mho. | | | | | p_H | | | Free acid $\times 10^6 N$ | | | Total acid $\times 10^6 N$ | | | a% | | |
|------|---|------|------|------|------|-------|------|------|------------------------------|------|------|-------------------------------|------|------|------------------------|------|-----|
| | 1° | 4° | 30° | 35° | 50° | 1° | 35° | 50° | 1° | 35° | 50° | 1° | 35° | 50° | 1° | 35° | 50° |
| T | | 31.3 | 51.0 | 57.0 | 69.8 | 4.15 | 4.19 | | 7.3 | 7.1 | | 10.5 | 10.0 | | 69.5 | 71.0 | |
| | | | | | | 4.12 | 4.11 | | | | | | | | | | |
| U | | | | | | 4.34 | 4.38 | 4.41 | 4.3 | 4.2 | 4.0 | 4.0 | 4.2 | 4.0 | completely dissociated | | |
| | | | | | | 4.39 | 4.39 | | | | | 4.0 | 4.0 | | | | |
| W | 33.0 | | | 76.5 | 96.0 | 3.86 | 3.85 | 3.85 | 13.8 | 13.8 | 14.1 | 17.4 | 17.8 | 18.2 | 79 | 77 | 57 |
| | | | | | | 3.86 | 3.86 | | | | | | | | | | |

It will be seen that a variation of temperature from 1° to 50° produces practically no change in the free and total acids. The amount of acid

FIG. 1.

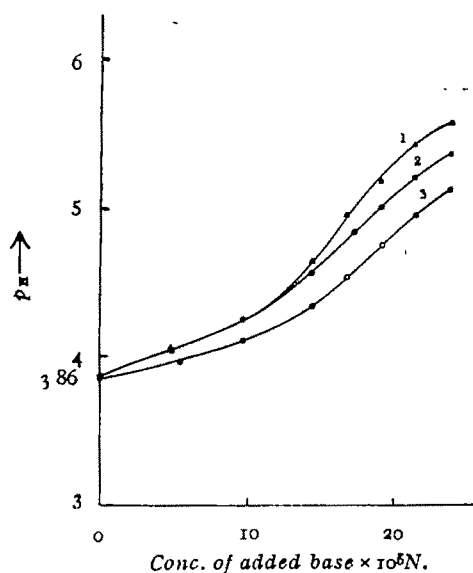


* A note on this subject has been published in this Journal, 1941, 18, 263.

neutralised at the inflexion point thus appears to be a fixed quantity. It has also been observed (Chatterjee, *loc. cit.*) that the total acid neutralised at the first inflexion point in the titration curves* with different bases is practically the same. The inflexion point acquires a special significance in this sense. The potentiometric titration curves of sols T and U (Fig. 1) at different temperatures practically coincide with one another. Those of sol W (Fig. 2) though giving almost the same total acidity at the inflexion points show a somewhat stronger buffer action with an increase in temperature.

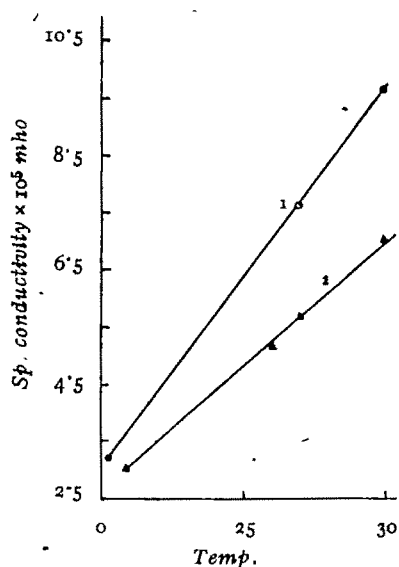
The specific conductivity changes linearly with temperature (Fig. 3). The temperature coefficient at 18° is 1.93 % in the case of sol T and 2.3 % with sol W. Pauli and Palmrich (*loc. cit.*) obtained similar linear variations between 0° and 90° and a temperature coefficient of about 2% at 18°.

FIG. 2.



Curves 1-3 refer respectively to titrations at 1°, 35° and 50°

FIG. 3.



Curves 1 and 2 refer respectively to sol W and sol T.

It appears from the data cited in Table V that the degree of dissociation of silicic acid sols do not change materially with temperature between 1° and 50°. The change in the degree of dissociation of an electrolyte having

* Titration curves of only sol U are given in Fig. 1.

the same concentration as sol W and 36-valent anion (p. 21) have been calculated using Onsager's equation (*loc. cit.*) and shown in Table VI.

TABLE VI.

| | | | |
|----------------------|----------|------|------|
| Temperature | ... 1° | 35° | 50° |
| Degree of dissn. (%) | ... 82.7 | 77.4 | 76.3 |

The calculated degree of dissociation is found to decrease with temperature. The effect of temperature on the degree of dissociation of silicic acid sols cannot, therefore, be explained from a consideration of Onsager's theory.

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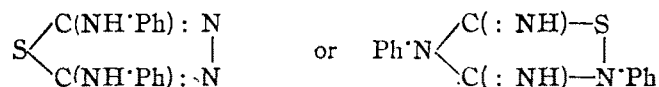
Received October 31, 1941.

PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD-N·C·S-. PART XI. OXIDATION OF PHENYLTHIOCARBAMIDE WITH COPPER SULPHATE, CUPRIC CHLORIDE, COPPER NITRATE, FERRIC CHLORIDE AND IODINE.

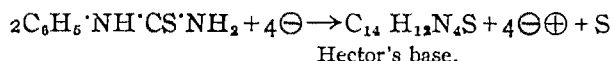
BY RAMCHANDRA SAHASRABUDHEY AND HANS KRALL.

Copper sulphate and cupric chloride have been found to be reduced by phenylthiocarbamide in acid medium with the simultaneous formation of complexes of the reduced salts. The reaction consists of two stages, primary and secondary. Primary reaction is independent of temperature, concentration of the reactions and dilution of the medium; the secondary change is largely influenced by temperature and is attended with the complex formation.

The present communication records an examination of the unexpected phenomenon observed by Lal and Krall (*J. Indian Chem. Soc.*, 1937, **14**, 477) that copper sulphate oxidises phenylthiocarbamide producing Hector's base (*Ber.*, 1889, **22**, 1176).



The action of oxidising agents has often been studied (for references *vide J. Indian Chem. Soc.*, 1939, **16**, 31). The general course of the reaction is as follows;



The present investigation has established that the reaction with copper sulphate or cupric chloride can be subdivided into primary and secondary changes. The primary change which consists in the reduction of the cupric salt to cuprous state by phenylthiocarbamide which itself undergoes oxidation to Hector's base is according to the general equation given above. Our experiments have shown that this change is independent of a change in the dilution of the medium, of concentration of the reactants and of temperature, but it takes place only in an acidic medium, the inherent acidity of the aqueous solutions of above copper salts being enough for the purpose. The secondary change which is largely influenced by temperature, takes place simultaneously with the primary one or closely

follows it, and consists in the formation of insoluble complexes of unchanged phenylthiocarbamide with the cuprous salts giving mostly $(\text{Ph.Thi})_3 \cdot \text{Cu}_2\text{SO}_4$ and $(\text{Ph.Thi})_3 \cdot \text{Cu}_2\text{Cl}_2$ at ordinary temperatures and $(\text{Ph.Thi})_3 \cdot \text{Cu}_2\text{SO}_4$ and $(\text{Ph.Thi})_3 \cdot \text{Cu}_2\text{Cl}_2$ at 100° . Amounts of copper in the complexes obtained at different temperatures agree with the composition of the compounds above described. Cupric salts do not themselves combine with phenylthiocarbamide. But in acidic media they oxidise a part of phenylthiocarbamide to Hector's base and the cuprous salts, so produced, immediately begin to combine with the unchanged phenylthiocarbamide to form insoluble complexes. This removal of phenylthiocarbamide as insoluble complexes acts as a limiting factor on the extent of the oxidative change. The nature of the complexes formed is influenced by temperature and so the temperature affects the net result of the changes in as much as that for every two molecules of cuprous sulphate formed either six or twelve of phenylthiocarbamide are removed in the form of complex. This is supported by the fact that previously prepared cuprous chloride forms a complex with phenylthiocarbamide in a quantitative manner.

It has been shown (Lal and Krall, *J. Indian Chem. Soc.*, 1937, **14**, 477) that silver nitrate combines with phenylthiocarbamide to form an insoluble complex and possibly it is the insolubility of this which prevents any oxidation-reduction in the case of silver nitrate.

Ferric chloride has been found to oxidise phenylthiocarbamide to Hector's base, itself undergoing reduction to colourless FeCl_2 . No complex appears to be formed in this case as the solution becomes colourless and shows only the turbidity due to precipitated sulphur on standing, but no bulky complex is precipitated and the reduced salt can be completely precipitated as Prussian blue with potassium ferricyanide.

Copper nitrate in aqueous solutions and aqueous iodine in acidic media have also been found to oxidise phenylthiocarbamide to Hector's base. These reactions are proposed to be investigated in further detail.

EXPERIMENTAL.

Copper Sulphate and Cupric Nitrate.—Known amount of phenylthiocarbamide was dissolved in water or the desired medium at the required temperature and dilution. A solution of copper sulphate (20%) was at once added and the mixture vigorously stirred. In the experiments conducted with solutions heated to boiling point the flame was removed after the addition of copper sulphate solution.

TABLE I.

| Ratio of the reactants Ph. Thi:CuSO ₄ (1/50th mole). | Dilution (c.c.). | Medium | Temperature. | Copper sulphate | | Copper used up for complex formation | SO ₄ used up for complex formation. | Atomic ratio in which Cu & SO ₄ are utilised for complex formation. | Hector's base expected to be formed as calculated on reduction. | Hector's base formed. | Percentage of initially present Ph. Thi. oxidised to Hector's base (calculated on reduction) | Percentage of Cu in complex. | Remarks. |
|--|------------------|-------------------------------------|--------------|-----------------|--------------------------|--------------------------------------|--|--|---|-----------------------|--|------------------------------|--|
| | | | | Copper present. | BO ₄ present. | | | | | | | | |
| 1:1 | 250 to 475 | Pure aqueous | 95°-100° | 1'2558. | 1'896g. | 0'6076g. | 0'4410g. | 213:100 | 0'62g. | 0'63g. | 23'1 | 17'66 | These figures correspond to the formation of the complex (Ph. Thi.) ₂ Cu ₂ SO ₄ with small quantities of the other complex (Ph. Thi.) ₂ ·Cu ₂ SO ₄ mentioned below |
| 1:2/3 | " | " | " | 0'8467 | 1'2787 | 0'5741 | 0'4447 | 196:100 | 0'625 | 0'62 | 23'3 | 17'6 | |
| 1:1/2 | " | " | " | 0'6254 | 0'9442 | 0'6254 | 0'4530 | 208:100 | 0'63 | 0'60 | 23'5 | 17'51 | |
| 1'46/100 | " | " | " | 0'5932 | 0'8988 | 0'5932 | 0'4249 | 210:100 | 0'61 | 0'61 | 22'7 | 17'5 | |
| 1'23/100 | " | " | " | 0'2974 | 0'4493 | 0'2974 | 0'2132 | 211:100 | 0'305 | 0'26 | 22'7 | | |
| 7/4 | " | " | " | 0'7172 | 1'0836 | 0'6134 | 0'4480 | 208:100 | 0'64 | 0'595 | 23'8 | 17'8 | |
| 2:3 | " | " | " | 1'9065 | 2'1248 | 0'6260 | 0'4532 | 208:100 | 0'64 | 0'585 | 23'8 | 17'95 | |
| 1:2 | " | " | " | 2'5015 | 3'777 | 0'6175 | 0'4510 | 227:100 | 0'64 | 0'59 | 23'8 | 17'6 | |
| 1:4 | " | " | " | 5'028 | 7'5930 | 0'6230 | 0'506 | 190:100 | 0'68 | 0'58 | 25'3 | | |
| 1:1 | 120 | " | " | 1'2714 | 1'9200 | 0'5856 | | | 0'61 | 0'58 | 22'8 | 17'2 | |
| 1:1 | 700 | " | " | 1'2714 | 1'9200 | 0'5936 | 0'4249 | 211:100 | 0'625 | 0'52 | 23'3 | 17'6 | |
| 1:1 | 330 | " | 40° | 1'2714 | 1'9200 | 0'3764 | 0'2850 | 200:100 | 0'40 | 0'43 | 14'6 | 11'96 | These figures correspond to the formation of the complex (Ph. Thi.) ₂ Cu ₂ SO ₄ chiefly. (Ph. Thi.) ₂ ·Cu ₂ SO ₄ is formed. |
| 1:1 | 450 | " | 20° | 1'2714 | 1'9200 | 0'3630 | | | 0'39 | 0'43 | 14'2 | 11'58 | |
| 1:1 | 900 | " | 8° | 1'2714 | 1'9200 | 0'3494 | | | 0'37 | 0'38 | 13'7 | 11'13 | |
| 1:1 | 250-475 | N-H ₂ SO ₄ | 95°-100° | 1'2714 | | 0'6016 | | | 0'63 | 0'595 | 23'5 | 17'6 | |
| 1:1 | " | N/10-H ₂ SO ₄ | " | 1'2504 | | 0'5944 | | | 0'625 | 0'62 | 23'2 | | |
| 1:1 | " | N-NH ₄ Ac | " | 1'2723 | | 1'2714 | nil | | nil | nil | | | |
| 1:1 | " | N-NaAc | " | 1'2714 | | 1'2714 | nil | | nil | nil | | | |
| 1:1 | 100 | Conc. HCl | 80°-85° | 1'2714 | 1'9200 | 0'8314 | nil | | 0'87 | 0'73 | 32'45 | 23'9 | |
| 1:1 | | | | | | | | | | | | | |
| 1:1 | | | | | | | | | | | | | |

A black residue of sulphides of copper is obtained and Ph·NH·CN is formed to the extent of 30% approximately. (Ph Thi.)₂Cu₂Cl₂ is formed.

TABLE I (Continued)

| Ratio of reactants Ph Thi Cu Cl ₂ (1/50th mole). | Dilution. | Medium. | Temperature. | Copper chloride | | Copper used up for complex formation. | Cl ₂ used up for complex formation. | Atomic ratio in which Cu & Cl ₂ are used for complex formation. | Hector's base expected to be formed as calculated on re- duction of CuCl ₂ to CuCl. | Hector's base formed | Percentage of initially present Ph. Thi. oxidised to Hector's base. | Percentage of copper in com- plex. | Remarks. |
|---|-----------|----------|--------------|-----------------|--------------------------|--|---|--|--|----------------------|---|---------------------------------------|---|
| | | | | Copper present. | Cl ₂ present. | | | | | | | | |
| 1:1 | 250c c. | Aq. | 95°-100° | 1.2664g. | | 0.7339g. | | 1:1 | 0.77g. | 0.73g. | 28.7 | 21.7 | A mixture of complexes (Ph·Thi) ₂ Cu ₂ Cl ₂ and (Ph·Thi) ₃ Cu ₂ Cl ₂ is formed. |
| " | " | N-HCl | " | 1.2714 | 1.4206g. | 0.7123 | | | 0.75 | 0.75 | 28.0 | | |
| " | 450 | Aq. | " | " | " | 0.7711 | | | 0.81 | 0.73 | 30.0 | | |
| " | 150 | Neutral | " | " | " | 0.7290 | 0.4148g. | 1:1 | 0.76 | 0.70 | 28.3 | 21.1 | The complex (Ph·Thi) ₃ Cu ₂ Cl ₂ is chiefly formed. |
| " | " | " | " | " | " | 0.7474 | 0.4148 | 1:1 | 0.79 | 0.72 | 29.4 | 21.5 | |
| " | 450 | " | 70° | 1.3119 | 1.465 | 0.6475 | | | 0.68 | 0.58 | 25.4 | | |
| " | 330 | " | 40° | " | " | 0.6339 | 0.3690 | 1:1 | 0.668 | 0.63 | 24.9 | 17.7 | The complex (Ph·Thi) ₃ Cu ₂ Cl ₂ is chiefly formed. |
| " | 450 | " | 20° | " | " | 0.6339 | 0.3598 | 1:1 | 0.668 | 0.612 | 24.9 | 18.8 | |
| " | 700 | N/10 HCl | 20° | " | " | 0.6338 | 0.3598 | 1:1 | 0.668 | 0.634 | 24.9 | 18.6 | |
| " | 900 | Aq. | 8° | " | " | 0.6204 | 0.3396 | 1:1 | 0.655 | 0.604 | 24.4 | 18.9 | Complex (Ph·Thi) ₃ Cu ₂ Cl ₂ is formed. |
| " | 100 | Neutral | 80°-85° | 1.2714 | | 0.8341 | | | 0.88 | 0.73 | 32.8 | 23.91 | |
| Ph. Thi : CuCl(1:1) | 50 | " | " | 1.2841 | | 1.2367 | | | nil | nil | nil | 23.93 | |

* The figures indicate that copper sulphate in the form of Cu₂SO₄ combines with phenylthiocarbamide. The quantities of Hector's base formed correspond to the copper reduced. More than one fourth of phenylthiocarbamide initially present is never oxidised to Hector's base. When temperature is changed a different complex is formed.

The mixture was allowed to cool to the room temperature and filtered. The complex was collected, washed, and dried at 100°-110°. The filtrate was treated with an excess of 10% ammonium hydrate solution, when on standing Hector's base granulated out. It was filtered, dried on a water-bath, and weighed on a tared filter. The copper and SO₄ were estimated in the filtrate as usual.

Copper in the complex was determined in oven-dried samples at 100°-110°, known weights of which were ignited and subsequently dissolved in concentrated nitric acid.

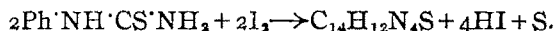
Copper nitrate gave similar results.

The results are given in Table I.

Cupric Chloride.—Chloride ions were estimated in the liquor by Volhard's method and copper determined as usual.

Ferric Chloride.—Phenylthiocarbamide (1.52 g.) was dissolved in boiling water (100 c.c.) and to the solution was added an equivalent of boiling ferric chloride solution. The yellow colour of the ferric chloride at once disappeared. After some time sulphur was deposited in the form of fine white powder. The solution was filtered and treated with an excess of potassium ferricyanide solution when an intense blue bulky precipitate of Prussian blue was obtained. It was filtered and from the clear yellow filtrate Hector's base was precipitated with ammonium hydrate, and identified through its m.p. and acyl derivative.

Iodine.—Aqueous iodine solution was gradually run into an acidified hot solution of phenylthiocarbamide. It became decolourised as soon as added and a pale yellow colouration developed when an excess was run in. The solution was filtered and from the filtrate Hector's base was precipitated as usual with aqueous ammonia. The reaction can probably be represented by the following equation :

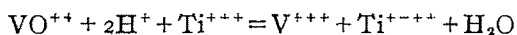


USE OF VANADOUS SULPHATE AS A REDUCING AGENT. PART IV. ESTIMATION OF TITANIUM

BY PARES CHANDRA BANERJEE.

Titanium has been estimated potentiometrically by measuring the changes in E. M. F (against N. C. E.) by titrating with a standard vanadous sulphate solution. The results are satisfactory and the accuracy of the method lies within 2 and 3%. In the presence of iron, three potential breaks are found in the titration curve: the first jump occurs in the reduction of Fe^{+++} to Fe^{++} , the second due to the reaction $\text{V}^{++++} + \text{V}^{++} = 2\text{V}^{+++}$ and the third owing to reaction of Ti^{++++} to Ti^{+++} .

The reaction between vanadous and titanium^{IV} salts does not appear to have been studied by any previous worker. It has been known for a long time that higher salts of vanadium, *viz.*, vanadic acid and vanadyl compounds are reduced by titanous salts.



A method based on these reactions has been described by Kolthoff and Furman for the potentiometric estimation of vanadium by titanous salts.

From theoretical consideration as well as from a study of the oxidation potentials of vanadium and titanium salts, it was anticipated that titanium^{IV} salts would be reduced by vanadous salts—a fact which has been verified by actual experiment. The oxidation potentials of the chain V^{II} to V^{III} , V^{III} to V^{IV} and V^{IV} to V^{V} are -0.2, +0.4 and +1.2 volts respectively while that of titanous salts (Ti^{III} to Ti^{IV}) is only 0.04 volt. Hence, titanium salts must be reduced by bivalent vanadium salt and since the oxidation potential of V^{III} to V^{IV} (+0.4) is greater than that of Ti^{III} to Ti^{IV} , V^{II} will not be oxidised beyond V^{III} ion. So, the reaction between the two salts takes place according to the equation,



The velocity of the reaction is rather slow at the ordinary temperature and it takes a long time for its completion. The velocity may, however, be increased by a rise in temperature when the reaction goes to completion in a relatively short time. If an excess of vanadous salt be added, the

reaction becomes complete even at the ordinary temperature within a reasonable period of time. Attempts were therefore made to utilise the above reaction for the volumetric estimation of titanium but without any success. This was due to the fact that chemical behaviour of either vanadous or titanous salt towards an indicator showed no difference. No suitable indicator was available which could be used to indicate the end-point. When the Ti salt was reduced with an excess of vanadous salt, the excess could not be estimated by any substance which would preferentially oxidise the V compound without any action upon the titanium salt. So ultimately this method of tackling the problem was abandoned.

Attempts were therefore made to perform the titration potentiometrically by measuring the changes in E. M. F. The results were satisfactory in sulphuric acid solution. If the work is carried out at room temperature, a long time elapses after each addition of reagent before the potential becomes constant. If the titration is made at 70-80° better results are obtained without difficulty. In the region of the end-point the last traces of titanium are reduced slowly so that one must wait a relatively longer time for the potential to become steady. Near the end-point, the titration must be done with slow addition of reagent otherwise an irregular and transient increase in E. M. F. may lead to erroneous results. The accuracy of the method was found to lie within 2-3%.

When the titanium solution contains iron, three potential breaks are found in the titration curve, the first jump occurs in the reduction of Fe^{III} to Fe^{II} ; the second due to the reaction, $\text{V}^{\text{IV}} + \text{V}^{\text{II}} = \text{V}^{\text{III}}$, and the third owing to the reduction of Ti^{IV} to Ti^{III} . It should be noted that during the process of titration of a mixture of iron and titanium, numerically the E. M. F. goes on decreasing, becomes equal to zero and then on interchanging the connections with the potentiometer, it begins to increase. This is due to fact that at the start, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ solution, which is positive, relative to the normal calomel electrode, is connected with the positive terminal (+E) of the potentiometer and the E. M. F. of the combination is therefore positive. After the reduction of iron and complete conversion of V^{IV} to V^{III} , the solution at once becomes negative to the calomel electrode which is now connected with the positive and the solution with the negative end of the potentiometer so that the E. M. F. of the combination becomes negative. So we may say that during the titration of a mixture of iron and titanium, the E. M. F. (against normal calomel electrode) continually goes on decreasing.

From the equation given above, it is evident that the equivalent weight of vanadous sulphate in the titration of titanium salts is equal to its mole-

cular weight. The strength of the reagent is therefore half the value obtained by standardising against ferric alum or dichromate, provided the salt is purely vanadous and absolutely free from vanadic salt. If the reagent contains some vanadic (V^{III}) salt the amount of V^{II} in the solution can be found out in the following way.

Suppose, P c.c. of the mixture containing x c.c. of vanadous (V^{II}) and y c.c. of vanadic (V^{III}) solution is equivalent to a c.c. of $0.1N$ ferric alum and b c.c. of $0.1N$ potassium permanganate solution. Then,

$$2x + y = a$$

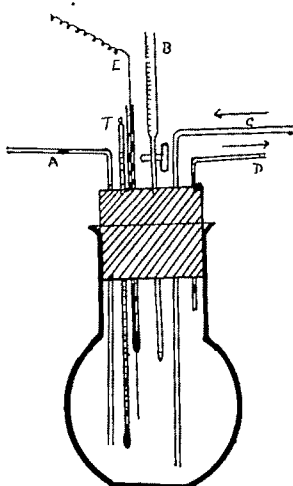
$$3x + 2y = b$$

whence, $x = 2a - b$. and $y = 2b - 3a$. These values of a and b are found out by titrating with ferric alum and permanganate respectively. Both V^{II} and V^{III} are oxidised to V^{IV} by ferric salts and to V^V by permanganate.

EXPERIMENTAL.

Pure potassium titanium fluoride (K_2TiF_6) (6.005 g.), twice recrystallised from hot water were dissolved in water and the solution made up

FIG. 1.



- A—Bridge connecting the N -calomel electrode.
 B—Burette. C—Inlet for CO_2 . D—Exit for CO_2 .
 E—Indicator electrode.
 T—Thermometer.

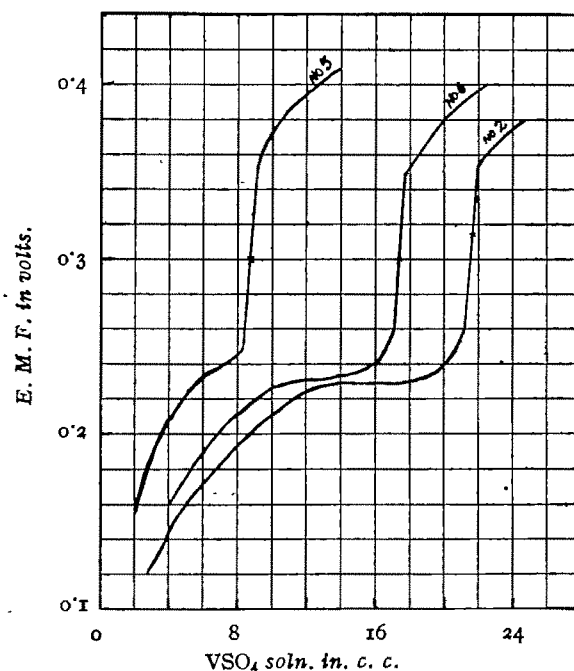
to 1 litre. An aliquot part of this solution was taken into the titration vessel (Fig. 1) which consists of a 250 c.c. flask closed with a six holed rubber stopper. The end of B passes through the middle hole; platinum electrode passes through another, through a third passes the siphon tube filled with normal potassium chloride and agar agar. Two other openings serve for the entrance and exit of carbon dioxide which is passed through the solution during titration. The thermometer T fills the remaining hole in the stopper. A few c.c. of concentrated sulphuric acid were added to the titanium solution which was then diluted with water to make it about $4N$ with respect to sulphuric acid. The solution was heated to about 80° and this temperature was maintained during titration by heating the flask with a micro burner. The end-point was determined from the titration curve (Fig. 2,) and the results of titration are given in Table I.

TABLE I.

 1 C.c. V^{++} -soln. = 1.366 mg. of Ti. Temperature = $75-80^{\circ}$.

| Ti-soln. taken. | H_2SO_4 added. | Total vol. | V-soln. reqd. | Titanium [found. calc.] |
|-----------------|------------------|------------|---------------|----------------------------|
| 25.0 c.c. | 10 c.c. | 100 c.c. | 21.4 c.c. | 29.22 mg 30.06 mg |
| 25.0 | 10 | 100 | 21.6 | 29.5 |
| 25.0 | 5 | 50 | 22.3 | 30.46 |
| 25.0 | 5 | 50 | 29.8 | 29.98 ,, |
| 10.0 | 5 | 50 | 8.70 | 11.88 12.024 |
| 20.0 | 10 | 100 | 17.25 | 23.56 24.048 |

[FIG. 2.



Analysis of a Mixture of Iron and Titanium.—25 C.c. of the standard titanium and 10 c.c. of iron alum solution of known strength were introduced into the titration vessel; 5 c.c. of concentrated sulphuric acid were added and the mixture diluted with water to about 50 c.c. The solution was heated to about 80° and titrated at this temperature with the vanadous

sulphate solution. Fig. 3 shows the titration curve of a mixture containing iron and titanium. Results of analysis are shown in Table II.

FIG. 3.

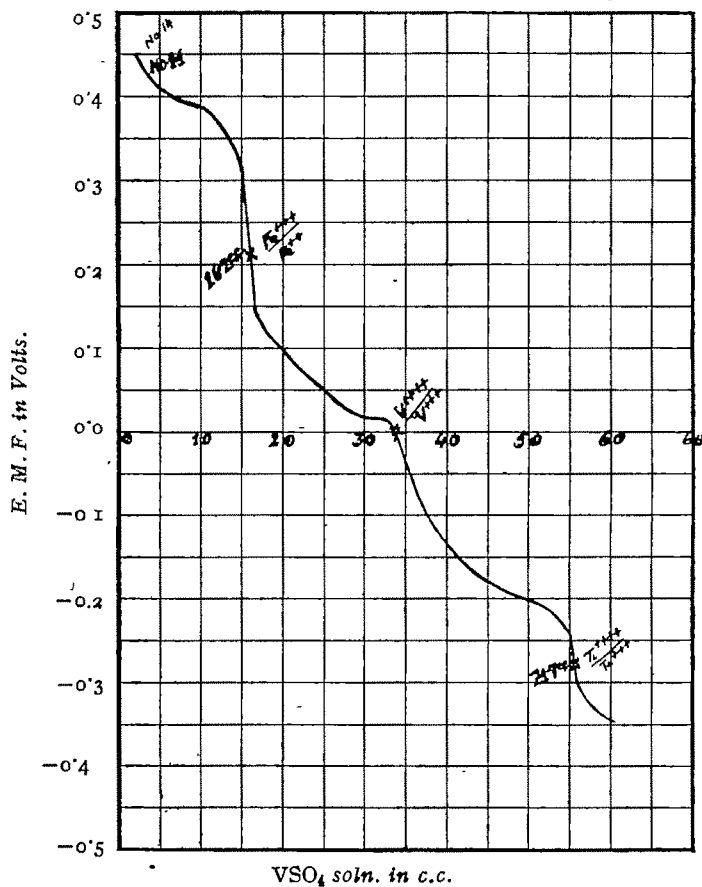


TABLE II.

1 C.c. of V^{++} -soln. = 1.366 mg. of Ti and 3.2 mg. of Fe.

| Fe. | V-soln. reqd. by Ti. | Iron | | Titanium | |
|-----------|----------------------|----------|-----------|-----------|-----------|
| | | found. | calc. | found. | calc. |
| 16.0 c.c. | 21.5 c.c. | 51.2 mg. | 52.08 mg. | 29.36 mg. | 30.06 mg. |
| 16.2 | 21.7 | 51.84 | 52.08 | 29.64 | 30.06 |

USE OF VANADOUS SULPHATE AS A REDUCING AGENT. PART V. ACTION OF VANADOUS SULPHATE UPON ORGANIC COMPOUNDS.

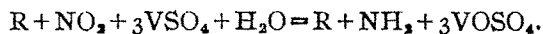
BY PAREŚ CHANDRA BANERJEE.

Some organic nitro compounds, such as, nitrobenzene, dinitrobenzene, *p*-nitroaniline, and picric acid and two organic dyes: indigo and methylene blue have been estimated by reducing the nitro group in the former cases with vanadous sulphate. A known weight of the nitro compound was treated with an excess of vanadous sulphate and after boiling for some time under a reflux in a current of carbon dioxide, the mixture was cooled and the excess of V^{++} solution was titrated with iron alum using sulphocyanide as indicator.

The powerful reducing action of vanadous salts is not confined to inorganic substances alone. A large number of organic substances belonging to both aliphatic and aromatic series are quantitatively reduced by bivalent vanadium salts. In these reactions, the reduction is more powerful and becomes complete much sooner at low acidities than at larger hydrogen ion concentration. So in many cases, in order to lower the acid concentration, Rochelle salt or sodium tartrate is added to the solution. Following pages contain an account of the estimation of some of these compounds.

Estimation of Nitro Compounds.

Reduction with Titanous Chloride.—The method described in this paper consists in the reduction of the nitro group with an excess of vanadous sulphate, followed by the determination of the excess with iron alum or any other suitable reagent. The reaction taking place may be represented by the equation,



In the reduction of the nitro group by Knecht-Hibbert method with titanous chloride it has been pointed out by Callan and Henderson (*J. Soc. Chem. Ind.*, 1920, 39, 86r) that although in many cases it gives excellent results, yet for certain substances *e.g.*, *o*-nitroanisole, α -mononitronaphthalene, etc. the method gives low results. This is attributed to the titanous chloride solution acting not only as a reducing agent but also as a chlorinating agent, simultaneously liberating hydrogen by substitution which, in addition, acts as a reducing agent. If, however, titanous sulphate is used, in place of titanous chloride, with these substances under similar conditions, correct results are obtained.

Reduction with Stannous Chloride.—One serious defect of this method is that chlorinated amino compounds are formed as readily during reduction with this substance as with titanous chloride, and consequently low results are obtained. Nitro compounds which are not chlorinated may be estimated by stannous chloride method as modified by Young and Swain (*J. Amer. Chem. Soc.*, 1897, **19**, 812) with a fair degree of accuracy.

Reduction with Vanadous Sulphate.—With vanadous sulphate which has for the first time been employed for the estimation of nitro group in organic compounds, no question of chlorination comes in. The reduction takes place in the presence of sulphuric acid and the results are obtained which are as accurate as with titanous sulphate. The method has been successfully used for the estimation of a number of nitro compounds, *e.g.*, nitrobenzene, nitroaniline, etc. A known weight of the nitro compound is treated with a large excess of V^{II} salt and after boiling for some minutes under a reflux in a current of carbon dioxide, the mixture is cooled and the excess of V^{II} salt is titrated with iron alum, using sulphocyanide as indicator. When a nitro compound which is easily volatile or volatile with steam, heating must be done under reflux, otherwise low results due to the loss of the nitro compound by volatilisation may be obtained (Callan and Henderson, *J. Soc. Chem. Ind.*, 1922, **41**, 1581.). In dealing with such substances, the reduction is carried out in a flask fitted with a short ground-in water condenser, a stream of carbon dioxide being supplied by a narrow glass tube passing down through the inner tube of the condenser to within a few centimetres of the surface of the liquid. Nitro compounds which are insoluble in water or in acids (*e.g.* nitrobenzene) is to be sulphonated with sulphuric acid, while nitro compounds which, like dinitrobenzene, are neither soluble in water nor easy to sulphonate may be dissolved in alcohol and added slowly to the hot solution of vanadous sulphate contained in a flask through which a current of carbon dioxide is maintained. For accurate estimations, care must be taken to use a large excess of vanadous sulphate, to boil the solution with the reducing agent and to maintain a current of carbon dioxide during the entire estimation. Reduction becomes complete only when these precautions are carefully observed.

EXPERIMENTAL.

Estimation of Nitrobenzene.—0.5023 G. of chemically pure redistilled (b.p. 208°) nitrobenzene was sulphonated by heating with 20 c.c. of fuming sulphuric acid on a water-bath for two hours and the solution was made up to 250 c.c. A measured volume of this solution was run to an

excess of vanadous sulphate and after boiling for some minutes in a current of carbon dioxide, the contents were cooled and the excess of vanadous sulphate titrated back with iron alum. In another series of experiments, instead of sulphonating, 0.3906 g. of nitrobenzene was dissolved in alcohol and the solution made up to 250 c.c. The reduction was effected by boiling an aliquot part under reflux with excess of vanadous sulphate.

TABLE I.

$$V^{++}\text{soln.} = 0.2N. \quad Fe^{+++}\text{soln.} = 0.1N.$$

$$1 \text{ C.c. of } 0.1N\text{-}V^{++}\text{soln} = \frac{C_6H_5NO_2}{6 \times 10^4} = 0.00205 \text{ g. } C_6H_5NO_2.$$

| Nitrobenzene taken. | V-soln. added. | Fe-soln. reqd. | Nitrobenzene found. | Remarks. |
|----------------------|----------------|----------------|---------------------|------------------------------------|
| 10 c.c.* (0.020092g) | 10 c.c. | 10.25 c.c. | 99.44% | After sulphonation. |
| 10 " " | 12 | 14.2 | 100.0 | |
| 10 " " | 15 | 20.25 | 99.4 | |
| 25 (0.05023) | 20 | 15.6 | 99.59 | Nitrobenzene dissolved in alcohol, |
| 25 " " | 20 | 15.55 | 99.78 | |
| 10 (0.015624) | 10 | 12.4 | 99.72 | |
| 10 " " | 10 | 12.4 | 99.72 | |
| 20 (0.031248) | 20 | 24.8 | 99.70 | |
| 25 (0.03906) | 20 | 20.95 | 99.99 | |
| 25 " " | 20 | 21.0 | 99.72 | |

* 10 c.c. contained 0.020092 g.

Estimation of Dinitrobenzene.—0.3374 G. of *m*-dinitrobenzene which was purified by recrystallisation from alcohol, was dissolved in alcohol and the solution made up to 250 c.c. A known volume of vanadous sulphate solution was measured into a conical flask, sulphuric acid was added, carbon dioxide passed over and a known volume of dinitrobenzene

solution run in. The mixture was boiled, allowed to cool and then titrated back with iron alum.

TABLE II.

V^{++} soln. = 0.2N. Fe^{+++} soln. = 0.1N.

$$1 \text{ C.c. of } 0.1N V^{++} \text{ soln.} = \frac{C_6H_4(NO_2)_2}{12 \times 10^4} = 0.0014 \text{ g. } C_6H_4(NO_2)_2.$$

| Dinitrobenzene taken. | V-soln. added. | Fe-soln. reqd. | Dinitrobenzene found. |
|-----------------------|----------------|----------------|-----------------------|
| 10 c.c.* | 12.5 c.c. | 15.4 c.c. | 99.60% |
| 10 | 15.0 | 20.45 | 99.04 |
| 10 | 15.0 | 20.4 | 99.60 |

* 10 c.c. contained 0.013496 g.

Estimation of p-Nitroaniline.—The substance was purified by crystallisation several times from alcohol and drying at 100°. 0.5405 G. of the pure product (m.p. 147°) were dissolved in sulphuric acid and made up to 250 c.c. with water. A measured volume of this solution was reduced with an excess of vanadous sulphate in the usual way and the excess titrated with iron alum.

TABLE III.

V^{++} soln. = 0.202N. Fe^{+++} soln. = 0.1N.

$$1 \text{ C.c. of } 0.1N V^{++} \text{ soln.} = \frac{C_6H_4NH_2NO_2}{6 \times 10^4} = 0.0023 \text{ g. } C_6H_4NH_2NO_2$$

| Nitroaniline taken. | V-soln. added. | Fe-soln. reqd. | p-Nitroaniline found |
|---------------------|----------------|----------------|----------------------|
| 10 c.c.* | 10 c.c. | 10.8 c.c. | 100.0% |
| 10 | 10.1 | 11.0 | 100.0 |
| 25 | 20.0 | 16.75 | 99.77 |
| 25 | 20.0 | 16.7 | 99.97 |

* 10 c.c. contained 0.02162 g.

Estimation of Picric Acid.—Picric acid (0.2928 g.) recrystallised several times from alcohol and having a melting point of 122.5° was dissolved in water and the solution made up to 250 c.c. A measured volume of vanadous sulphate was added to a known volume of this solution acidified with sulphuric acid, boiled for 10 to 15 minutes in a current of carbon dioxide and after cooling the excess of vanadous sulphate, titrated with iron alum.

TABLE IV.

$$V^{++} \text{ soln.} = 1.48 \text{ N}/10. \quad Fe^{+++} \text{ soln.} = 0.1 \text{ N.}$$

$$1 \text{ C.c. of } 0.1 \text{ N } V^{++} \text{ soln.} = \frac{C_6H_5OH(NO_2)_3}{18 \times 10^4} = 0.001272 \text{ g. picric acid.}$$

| Picric acid taken. | V-soln. added. | Fe-soln. reqd. | Picric acid found. |
|--------------------|----------------|----------------|--------------------|
| 10 c.c.* | 20.0 c.c. | 20.4 c.c. | 99.93% |
| 15 | 12.6 | 9.5 | 99.4 |
| 15 | 20.0 | 15.85 | 99.6 |
| 25 | 25.0 | 14.05 | 99.7 |
| 25 | 30.0 | 21.5 | 99.5 |

* 10 c.c. contained 0.011712 g.

Estimation of Indigo.—Indigo has been estimated by titrating the sulphonated dyestuff, $C_{16}H_8N_2O_2(SO_3H)_2$, with vanadous sulphate in the presence sodium tartrate in an atmosphere of carbon dioxide.

Finely ground pure indigo, 1.624 g., (Kahlbaum, *pro analysi*) was mixed with 10 c.c. of concentrated sulphuric acid and heated in a water-bath at about 100° for an hour. The contents of the vessel were then cooled and dissolved in water and made up to 250 c.c. A known volume of this solution and about 50 c.c. (20%) of sodium tartrate solution were introduced into a conical flask fitted with a rubber stopper having three holes. Through one of these holes a current of carbon dioxide was introduced, another was fitted with a tube for the escape of the gas and a third was for adding the vanadous sulphate solution from the burette. This precaution was necessary to prevent the oxidation of indigo white by air.

TABLE V.

$$V^{++} \text{ soln.} = 0.5882 \text{ N}/10.$$

$$1 \text{ C.c. of } 0.1 \text{ N } V^{++} \text{ soln.} = \frac{C_{16}H_{10}N_2O_2}{2 \times 10^4} = 0.0131 \text{ g. of indigo.}$$

| Indigo taken. | V-soln. reqd. | Indigo found. |
|---------------|---------------|---------------|
| 10 c.c.* | 8.4 c.c. | 99.65% |
| 10 | 8.35 | 99.06 |
| 20 | 16.70 | 99.06 |
| 25 | 20.90 | 99.15 |
| 25 | 20.90 | 99.15 |

* 10 c.c. contained 0.06496 g.

The solution was boiled and the hot solution titrated with V^{++} -solution until the blue colour of indigo disappeared.

Estimation of Methylene Blue.—Pure recrystallised methylene blue (2.3226 g.) free from zinc chloride was dissolved in water and the solution made up to 500 c.c. 50 C.c. of this solution was measured into a conical flask, a small quantity of hydrochloric acid was added, carbon dioxide was passed into the flask in the manner described for indigo, and the contents were heated to boiling. The hot solution was then titrated until the blue colour just disappeared.

TABLE VI.

$$V^{++}\text{-soln.} = 1.46 N/10.$$

$$1 \text{ C.c. of } 0.1N V^{++} \text{ solution} = \frac{C_{16}H_{18}N_3SCl}{2 \times 10^4} = 0.015975 \text{ g. methylene blue.}$$

| Methylene blue taken. | V-soln. reqd. | Methylene blue found. |
|-----------------------|---------------|-----------------------|
| 50 c.c. * | 9.90 c.c. | 99.4% |
| 50 | 9.95 | 99.91 |
| 50 | 9.90 | 99.4 |
| 50 | 9.85 | 98.91 |
| 50 | 9.90 | 99.4 |

* 50 c.c. contained 0.23226 g.

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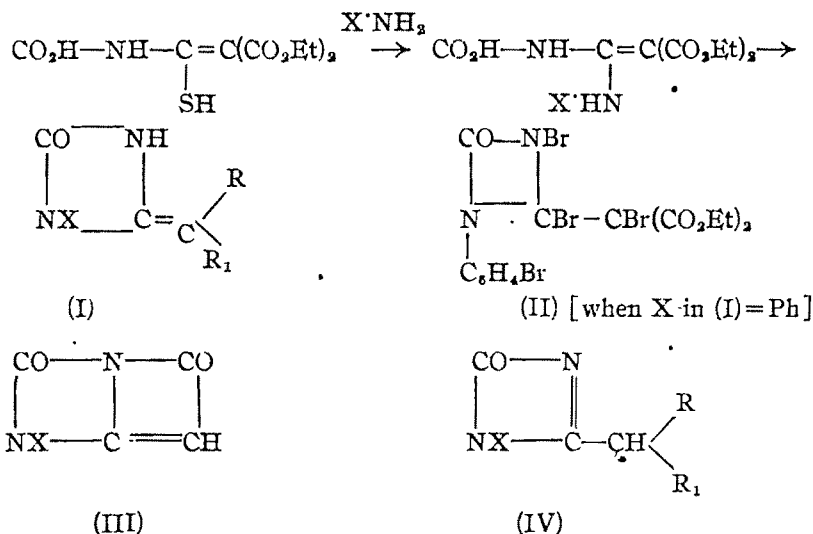
SYNTHESIS OF SOME FOUR-MEMBERED HETEROCYCLIC COMPOUNDS.*

BY TEJENDRA NATH GHOSH AND DEBABRATA DAS-GUPTA.

By reacting dicarbethoxythioacetocarbamie acid with an aromatic amine a four-membered heterocyclic compound, with alternate carbon and nitrogen atoms, has been obtained. The constitution of this heterocyclic compound has been established by preparing some derivatives and studying their properties. This compound has been found to undergo an isomeric change due to the migration of a hydrogen atom from nitrogen to carbon.

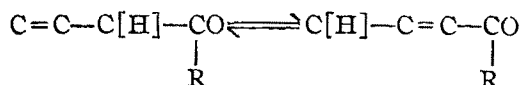
It has been observed (Ghosh, *J. Indian Chem. Soc.*, 1936, 13, 86; 1938, 15, 89) that thioacetocarbamie acid derivatives are characterised by their pronounced reactivity towards hydrazines and diamines and as such are of considerable value for synthetic purposes. The general mechanism of these reactions is that sulphuretted hydrogen is first eliminated and then ring-closure is effected by the elimination of either alcohol or water. Dicarbethoxythioacetocarbamie acid has now been similarly found to react readily with an aromatic amine to yield a four-membered heterocyclic compound (I, $R=R_1=CO_2Et$) with alternate carbon and nitrogen atoms. The structure (I, $R=R_1=CO_2Et$) is supported by the fact that the compound is readily soluble in alkali, yields an acetyl derivative and decolourises bromine yielding a colourless tetrabromo derivative which is tentatively assigned the structure (II) (cf. Farooq and Hunter, *J. Indian Chem. Soc.*, 1932, 9, 546). The compound (I, $R=R_1=CO_2Et$) is easily decomposed by acid or alkali, the aromatic amine being one of the degradation products. With hydrazine hydrate it yields the monohydrazide (I, $R=CO_2Et$; $R_1=CONHNH_2$). The presence of the hydrazino group has been established by the formation of benzylidene and phenylthiosemicarbazide derivatives with benzaldehyde and phenyl isothiocyanate respectively. When treated with sodium ethoxide, the compound (I, $R=R_1=CO_2Et$) yields (III). That the compound (III) does not contain any carbethoxy group has been established. The compound (III) may be regarded as a bridged pyrimidine derivative.

* Note published in *Science and Culture*, 1940, 5, 494.



When heated at 165° - 170° , the compound (I, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) isomerises to (IV, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) due to the migration of a mobile hydrogen atom. Whereas the compound (I, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) gives a deep red colouration with ferric chloride (*cf.* Frerichs and Hartwig, *J. ph. Chem.*, 1905, ii, 72, 489) and readily decolourises bromine and potassium permanganate solution, (IV, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) does not give any distinctive colouration with ferric chloride and does not decolourise bromine or potassium permanganate solution. The compound (IV, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) yields a dianilide, and is hydrolysed to the acid (IV, $\text{R}=\text{H}$; $\text{R}_1=\text{COOH}$) with alkali, which shows that the compound is more stable than (I, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$). So far as the compounds (I and IV, $\text{R}=\text{R}_1=\text{CO}_2\text{Et}$) are concerned, it appears that a relationship exists between the internal strain in the ring due to the presence of a double bond just outside the ring and the tendency of the double bond to become saturated by the migration of the mobile hydrogen atom, thus making the ring more stable (*cf.* Kon and Speight, *J. Chem. Soc.*, 1926, 2727).

The above isomeric change resembles the pentad-enol system,



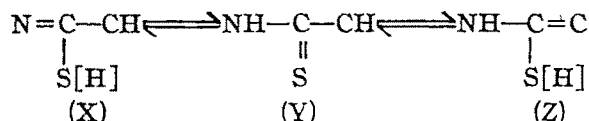
which has been studied extensively by Kon, Linstead and their collaborators. Reference is also made in this connection to imino-enamine system, $\text{C}(\text{H})-\text{C}=\text{N} \rightleftharpoons \text{C}=\text{C}-\text{N}(\text{H})$, studied by Ponzio and Torres (*Gazzetta*, 1929, 59, 461).

It is recognised that the closure of a four-membered heterocyclic ring from an open-chain molecule is, in general, one of the most difficult operations in ring-formation. Ingold and Piggott (*J. Chem. Soc.*, 1922, 121, 2794) obtained 1:3-dimethindiazine rings. Senier and Shephard (*J. Chem. Soc.*, 1909, 98, 594) obtained methylene diphenylcarbamide, which is hydrolysed by boiling water. For other four-membered heterocyclic compounds with alternate carbon and nitrogen atoms, reference is made to the work of Lippmann and Regensdorfer (*Ber.*, 1897, 30, 2056).

The active tautomerism of the system, $>C(H)-C=S \rightleftharpoons >C=C-S(H)$, is well known and has been observed in thioketones (Mitra, *J. Indian Chem. Soc.*, 1931, 8, 472). A compound, containing the group-

ings $(NH-CS)$ and $\begin{matrix} R \\ R^1 \end{matrix} \rangle CH-CS$ (where R and R^1 are strongly negative

groups), should exhibit the characteristic feature of a tautomeric body because of the presence of two mobile hydrogen atoms. The tautomeric nature of dicarbethoxythioacetocarbamic acid has been adequately borne out by the various reactions studied. From a study of its condensation products with phenylhydrazine, *o*-phenylenediamine (Ghosh, *loc. cit.*), and with an aromatic amine, as described in this paper, evidence is brought forward to show that dicarbethoxythioacetocarbamic acid shows a remarkable tendency for tautomerism in a system.



the form (Y) being considered the central phase from which (X) and (Z) originate depending upon which of the two mobile hydrogen atoms tautomerises. In the above equilibrium, one particular form predominates depending upon the nature of the reactant

EXPERIMENTAL.

N-Phenyl-*N*:*N*¹-dicarbethoxyvinyleneurea (I, $X=Ph$; $R=R_1=CO_2Et$).—Aniline (7.4 g.) was added to an alcoholic solution of dicarbethoxythioacetocarbamic acid (21 g., prepared according to the method of Ghosh and Guha, *J. Indian Inst. Sci.*, 1933, 16A, 103), when the reaction immediately commenced with evolution of sulphuretted hydrogen and rise in temperature. The reaction mixture was heated under reflux for about 2 hours,

cooled and diluted with water, when a heavy oil was obtained, which soon solidified. The solid was first washed with very dilute hydrochloric acid, then aqueous sodium bicarbonate solution and finally with water. It was crystallised from dilute alcohol in colourless shining prisms, m.p., 74-75°. (Found : C, 56.28 ; H, 5.31 ; N, 8.65. $C_{15}H_{18}O_5N_2$, H_2O requires C, 55.90 ; H, 4.96 ; N, 8.69 per cent). It does not dissolve in bicarbonate solution even on long standing but is readily soluble in alkali. It readily decolourises bromine water.

Bromo Derivative (II).—Bromine was slowly added to a cold acetic acid solution of the above compound. Each drop of bromine became instantly decolourised and a crystalline solid slowly came out which crystallised from absolute alcohol in colourless shining needles, m.p., 120-21°. (Found : N, 4.49 ; Br, 51.03. $C_{15}H_{14}O_5N_2Br_4$ requires N, 4.50 ; Br, 51.44 per cent). It is insoluble in cold dilute alkali and remains unchanged when triturated with cold dilute alkali for a long time, which shows that the compound is not a hydrobromide.

N-p-Tolyl-N : N¹-dicarbethoxyvinyleneurea (I, X = p-tolyl ; R = CO_2Et ; $R_1 = CONH-NH_2$).—The method of preparation was the same as in the case of the previous compound. The reaction product crystallised from dilute alcohol in colourless shining prisms, m.p. 61-62°. (Found : N, 8.28. $C_{16}H_{18}O_5N_2$, H_2O requires N, 8.33 per cent). It is insoluble in sodium bicarbonate solution but readily soluble in alkali.

N-Phenyl-N : N¹-(carbethoxy-carbohydrazidovinylene)-urea (I, X = Ph ; R = $R_1 = CO_2Et$)—An alcoholic solution of the above compound and excess of hydrazine hydrate was heated on the water-bath for about 30 minutes and kept overnight at room temperature. On dilution with water, a semi-solid mass was obtained which was next treated with dilute alkali. A very small quantity of an alkali-insoluble compound was obtained, which crystallised from alcohol in colourless slender needles, m.p., 231-32°.

The alkaline solution, on acidification, gave a solid which crystallised from alcohol in colourless needles. It melts at 171° with instantaneous formation of a solid (colourless prismatic needles), melting at 252-53° (decomp.). (Found : N, 19.19. $C_{13}H_{14}O_4N_4$ requires N, 19.31 per cent).

The above compound reacts readily with phenyl isothiocyanate when heated in alcoholic solution to yield the *phenylthiosemicarbazide derivative* which crystallised from large quantity of alcohol in colourless rectangular plates, m.p., 188-89° (decomp.). It is soluble in cold alkali and is easily desulphurised by yellow oxide of mercury. (Found : N, 16.28. $C_{20}H_{19}O_4N_3S$ requires N, 16.47 per cent).

Benzylidene Derivative.—An acetic acid solution of equimolecular pro-

portions of the above compound (I, $X=Ph$; $R=CO_2Et$; $R_1=CO NH \cdot NH_2$) and benzaldehyde was heated under reflux for about 15 minutes when a crystalline solid (colourless plates) came out. As it was found to be practically insoluble in alcohol, acetic acid and other solvents, it was washed several times with acetic acid and alcohol and was found to melt at $209^{\circ}-10^{\circ}$ (decomp.). (Found: N, 14.35. $C_{20}H_{18}O_4N_4$ requires N, 14.81 per cent).

5-Phenyl-1:5-diazo-(0, 2, 2)-bicyclo- Δ^3 -hexene-2:6-dione* (III, $R=Ph$).—Sodium (1.1 g.) was dissolved in 100 c.c. of absolute alcohol. After the evolution of hydrogen had ceased, 15 g. of the compound (I, $X=Ph$; $R=R_1=CO_2Et$) were added to the solution and the clear solution was heated under reflux in an oil-bath for about 3 hours, when a solid was precipitated. The solution was allowed to cool and further quantity of the reaction product was obtained by dilution with water. It crystallised from alcohol (Norit), in which it is sparingly soluble, in colourless shining rectangular plates, m.p., $245-46^{\circ}$, yield 5 g. (Found: N, 15.17. $C_{16}H_{10}O_2N_2$ requires N, 15.05 per cent). It is readily soluble in glacial acetic acid and the solution decolourises potassium permanganate solution. It does not give any anilide or any hydrazide and is unaffected by 10-15% alcoholic potash; indicating thereby that the compound does not contain any carbethoxy group. It is insoluble in cold dilute hydrochloric acid and also in cold dilute alkali.

It yields an unstable yellow bromo derivative, which, on treatment with water, yields an almost colourless solid. The latter compound, which contains bromine, shrinks at 130° , slowly turns dark and resinifies above 200° , and could not be obtained in a pure state.

N-Phenyl-N¹:N¹-dicarbethoxy-ethenylurea (IV, $X=Ph$; $R=R_1=CO_2Et$).—The above compound (I, $X=Ph$; $R=R_1=CO_2Et$, 10 g.) was heated in an oil-bath at $165^{\circ}-170^{\circ}$ for about 3 hours. The pasty yellowish mass was cooled and triturated with alcohol, when a solid was obtained, which crystallised from alcohol in colourless shining rectangular plates, m.p. $168-70^{\circ}$, yield 5 g. (Found: C, 58.88; H, 5.74; N, 9.11. $C_{15}H_{16}O_6N_2$ requires C, 59.21; H, 5.26; N, 9.21 per cent). It is soluble in cold dilute alkali, and in cold concentrated hydrochloric acid from which the substance is precipitated unchanged as colourless slender needles on dilution with water. It is insoluble in ether.

The above transformation can also be effected by heating the compound (I, $X=Ph$; $R=R_1=CO_2Et$) at $125^{\circ}-130^{\circ}$ in *vacuo* for about 6-7 hours,

* Nomenclature of this compound and of other compounds described in this paper has been adopted according to the system followed in "The Ring Index" by Patterson and Capell, 1940.

when the water of crystallisation is removed. A solid with a yellow tinge is slowly formed, which, on crystallisation, has been found identical with the above compound (IV, X=Ph ; R=R₁=CO₂Et) (mixed m.p.).

Dianilide.—When a mixture of aniline (2.5 g.) and the above compound (IV, X=Ph ; R=R₁=CO₂Et, 4 g.) was heated in an oil-bath at 160°-165°, there was profuse evolution of alcohol and in about 15 minutes a crystalline solid came out. After washing with alcohol, the solid was crystallised from glacial acetic acid in colourless, shining, rectangular plates, m.p. 236°-38°, yield 3 g. (Found : N, 14.26. C₂₀H₁₈O₃N₄ requires N, 14.07 per cent). It is sparingly soluble in alcohol and insoluble in cold dilute alkali.

N-Phenyl-N : N¹-carboxyethylurea (IV, X=Ph ; R=H ; R₁=CO₂H).—A solution of the above compound (IV, X=Ph ; R=R₁=CO₂Et, 6 g.) in 10% alcoholic potash was heated under reflux on the water-bath for about 8 hours. Alcohol was distilled under reduced pressure and the solid was dissolved in water, filtered from any suspended impurities and just acidified with acetic acid. The precipitated solid was purified by dissolving in aqueous sodium bicarbonate and acidification with acetic acid. It was crystallised from alcohol in almost colourless rectangular plates. It turns brown on heating and does not melt even at 300°, yield 0.8 g. (Found : N, 13.29. C₁₀H₈O₃N₂ requires N, 13.72 per cent).

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CONDENSATION OF *o*-, *m*-, AND *p*-NITROBENZALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

BY DIL BAHAR SINGH MITTAL.

Aldehydes have been condensed with malonic acid using a mixture of pyridine (1 mol.) and piperidine (traces) by Haworth, Perkin and Rankin (*J. Chem. Soc.*, 1924, 128, 1693) and by Dutt (*J. Indian Chem. Soc.*, 1925, 1, 297) and a few other bases each in molecular proportions (Dalal and Dutt, *ibid.*, 1932, 9, 309). The pyridine-piperidine method, originally given by Haworth, Perkin and Rankin (*loc. cit.*) and modified by Robinson and Shinoda (*J. Chem. Soc.*, 1924, 1693) has been applied by Chakravarti, Haworth and Perkin, who using *m*-methoxybenzaldehyde and malonic acid (1 : 3 mols.) in pyridine (3.5 mols.) and a trace of piperidine (5 c.c. in 250 c.c. of pyridine with 100 g. of aldehyde and 160 g. of malonic acid) report "an almost quantitative yield" on heating.

Work in these laboratories has shown that such excessive proportions of the base and of malonic acid are not essential and that these condensations are, as well, even much better carried out, when for one molecule of the aldehyde, only one of the acid and 0.15-0.25 mol. of pyridine or a similar base are used (Kurien and Pandya, *J. Indian Chem. Soc.*, 1934, 11, 824; Ali, Kurien and Pandya, *Proc. Indian Acad. Sci.*, 1935, 1A, 440; Pandya and Vahidy, *ibid.*, 1935, 2A, 402; 1936, 4A, 134, 140, 144; 1937, 5A, 437, 181).

It has been generally found that not only does the condensation take place very easily but also that the product is much purer and is obtained in greater yields, which are often quantitative. It has also been observed that the action of the base is truly catalytic as even in its absence the reaction proceeds, but very slowly and the yields are much less.

In this paper the condensations of *o*-, *m*-, and *p*-nitrobenzaldehydes have been studied under the same conditions. Dalal and Dutt (*loc. cit.*) obtained *o*-nitrocinnamic acid by heating a mixture of *o*-nitrobenzaldehyde and malonic acid for 9 hours on a water-bath in the presence of quinoline (mol. proportion), but the yield was only 44.4%.

Dutt (*J. Indian Chem. Soc.*, 1925, 1, 300) condensed *m*-nitrobenzaldehyde and malonic acid in the presence of pyridine (1 mol.) and traces of piperidine in 90% yield. Dalal and Dutt (*loc. cit.*) obtained the same acid

in 82.5% yield by heating for $3\frac{1}{4}$ hours on a water-bath in the presence of quinoline (molecular proportion).

Dutt (*loc. cit.*) obtained from *p*-nitrobenzaldehyde and malonic acid *p*-nitrocinnamic acid in 82% yield, using pyridine (1 mol.) and traces of piperidine. Datta and Dutt (*loc. cit.*) obtained the same acid in about 75% yield by heating *p*-nitrobenzaldehyde and malonic acid for 3 hours on a water-bath in the presence of quinoline.

EXPERIMENTAL.

The condensations were carried out exactly following the method of Pandya (*J. Indian Chem. Soc.*, 1934, **11**, 824, *et. seq.*).

TABLE I.

| Catalyst | Amount of catalyst = 0.15 mol. | | |
|-----------------|--------------------------------|------------------|------------------|
| | <i>o</i> -Nitro- | <i>m</i> -Nitro- | <i>p</i> -Nitro- |
| 1. Pyridine | 1.75 g. (90.67%) | 1.70 g. (80.08%) | 1.69 g. (87.56%) |
| 2. Piperidine | 1.75 (88.08) | 1.65 (85.49) | 1.64 (84.97) |
| 3. Quinoline | 1.60 (82.90) | 1.55 (80.35) | 1.45 (75.12) |
| 4. Without base | 1.00 (51.80) | 1.02 (52.84) | 1.00 (51.85) |

The products from *o*- and *m*-nitrobenzaldehyde are colourless and the product from *p*-nitrobenzaldehyde is light yellow in colour in all these cases.

Thus *o*-, *m*-, and *p*-nitrobenzaldehydes undergo condensation with malonic acid very readily on heating on the water-bath and the reaction is very nearly completed in 4 hours in the presence of a trace of pyridine, piperidine and quinoline but it takes a much longer time in the absence of any base, when the yield in 4 hours comes up to about 40% only.

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A NOTE ON THE 'KINETIC' EQUIVALENCE OF BROMINE ATOMS IN PHOSPHORUS PENTABROMIDE.

BY S. D. CHATTERJEE.

Using radioactive bromine as indicator, it has been found that the five bromine atoms in PBr_5 are functionally equivalent.

Roginsky and Gopstein (*Phys. Z. Sowjetunion*, 1935, 7, 672) investigated the kinetic equivalence of bromine atoms in cupric bromide which decomposed when heated to the cuprous compound. They started with radioactive cupric bromide (CuBr_2^*) and effected its decomposition at 250° . The cupric salt was reformed at 100° in the presence of inactive bromine vapour. A 50% decrease in activity was obtained as a net result of such a series of steps. On repeating the cycle, however, five times, about 50% of the original activity still remained instead of about three per cent as is to be expected. Apparently, the bromine atoms in cupric bromide are not equally reactive.

The object of the present experiment was to test whether the above results are true for the phosphorus pentabromide molecule. It is well known that phosphorus pentabromide is formed by mixing theoretical proportions of phosphorus tribromide and bromine. On the other hand, when phosphorus pentabromide is heated, it melts to a red liquid forming a mixture of phosphorus tribromide and bromine at 100° , and the pentabromide is reformed on cooling. According to Baudrimont, if CO_2 be passed into a bulb containing the pentabromide heated to a water-bath, bromine passes off and the tribromide remains.

EXPERIMENTAL.

PBr_5 (7 c.c.) was shaken with about 150 c.c. of slow neutron-irradiated ethyl bromide. The ethyl bromide was removed by distillation and the radioactive PBr_5 remained as a residue. Its activity was measured by the liquid in a thin double-walled glass vessel and slipping it over a thin-walled G-M counter. Measurements were commenced when most of the 18 min. activity had decayed.

PBr_5 was next transferred to a glass vessel containing two side-tubes and cooled in an ice-bath. About 3.5 c.c. of Br_2 were added gradually, when crystals of PBr_5 separated out. The vessel with PBr_5 crystals was then heated on a water-bath at 100° , when PBr_5 readily decomposed into

PBr_3 and Br_2 . Br_2 was chased out by means of dry CO_2 and absorbed in a dilute solution of sodium hydroxide. The activity of PBr_3^* and NaBr^* were then successively measured. It was found that the activity appearing in the compounds was roughly proportional to the weight of bromine atoms contained in PBr_3 and Br_2 . The reaction may be represented as follows :



where the asterisk denotes the radioactive constituent.

In a second series of experiments radioactive phosphorus pentabromide was prepared by exchanging PBr_5 with irradiated $\text{C}_2\text{H}_5\text{Br}$. Radioactive PBr_5 was then decomposed into PBr_3 and Br_2 , roughly proportional amounts of activity appearing in the compounds. This indicates that all the bromine ions in phosphorus pentabromide are functionally equivalent. A similar result has been reported by Grinberg (*Bull. Acad. Sci. U. R. S. S. Ser. Phys.*, 1940, 4, 342) who investigated the following reaction :



Incidentally, it was also found that if the compounds PBr_3 and PBr_5 are taken, containing equal amounts of bromine and are exchanged with equal amounts of neutron-irradiated ethyl bromide, the activity appearing in PBr_5 was much greater than in the case of PBr_3 . Measurement of activity in both cases was done in inactive ethyl bromide solution of same volume under practically identical conditions. Considering the difference in two cases, one may, therefore, suggest that the strength of chemical binding of bromine atoms in PBr_5 is greater than in the case of PBr_3 .

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ON RELATIONSHIPS BETWEEN VISCOSITY AND SURFACE TENSION OF LIQUIDS.

BY R. C. TRIPATHI.

A number of equations connecting viscosity and surface tension, obtained by combining (a) equations connecting viscosity and density with or without temperature on one hand and (b) Macleod's equation connecting surface tension and density on the other, has been examined. The simplest and one of the most successful equation is found to have the form, $\log \log \eta = m\gamma^{\frac{1}{4}} + c$.

Buehler (*J. Phys. Chem.*, 1938, **42**, 1207) has combined Mott Sauder's equation (*J. Amer. Chem. Soc.*, 1931, **53**, 154) $\log \log \eta = md - 2.9$ with Sugden's well-known parachor equation (*J. Chem. Soc.*, 1924, **126**, 1177);

$$P = \frac{M}{d} \gamma^{\frac{1}{4}}.$$

In Mott Sauder's equation viscosity is to be taken in centipoises, m is a constant characteristic of each liquid and further mM which is denoted by I is an additive function. Hence the equation obtained by Buehler is

$$\log \log \eta = \frac{I}{P} \gamma^{\frac{1}{4}} - 2.9.$$

Buehler shows the value of I/P should on the average, be 1.2. Therefore his equation assumes the form $\log \log \eta = 1.2 \gamma^{\frac{1}{4}} - 2.9$. He claims that this equation connecting viscosity and surface tension is better than the one advanced by Silvermann and Roseveare (*J. Amer. Chem. Soc.*, 1932, **54**, 4460): $\eta^{-1} = k\gamma^{-\frac{1}{4}} + c$. His claim does not seem to be justified as Table I. will show. Associated liquids are not included in this table because Buehler does not claim that his equation could be applied to them.

TABLE I.

| Liquid. | Temp. range. | γ range γ max.- γ min. | Constants of Silvermann and Roseveare's equation. | | Silvermann and Rose- veare's eq. | Maximum % diff. Buehler's equation. |
|------------------|-----------------|---|--|----------------------|--|---|
| | | | $K \times 10^{-3}$. | $C \times 10^{-3}$. | | |
| CCl_4 | 20-170° | 17.15 | 3.500 | -1.400 | 5.0 | 33.2 |
| Chlorobenzene | 20-160 | 15.76 | 4.180 | -1.610 | 3.2 | 11.0 |
| Toluene ... | 0-110 | 12.15 | 4.930 | -1.966 | 3.9 | 4.7 |
| Acetone ... | -71-56 | 16.20 | 5.170 | -2.052 | 3.0 | 4.5 |
| Benzene . | 0-100 | 13.85 | 4.465 | -1.772 | 7.4 | 12.15 |
| Ether ... | -95-0 | 12.78 | 4.770 | -1.942 | 1.3 | 18.6 |
| <i>p</i> -Xylene | 10-130 | 13.00 | 4.500 | -1.773 | 2.1 | 3.1 |

TABLE II.

| Liquid. | Temp. range. | Constants. | | | | | | | |
|---------------------------|--------------|---|----------------------|------------------------------------|--------|------------------------------------|---|------------------------------------|--|
| | | Silvermann and Roseveare's equations. | | Buehler's modified equation. | | Maximum % difference | | | |
| | | $K \times 10^{-4}$. | $C \times 10^{-4}$. | m . | C . | Buehler's modified equation. | Silverman and Roseveare's equation. | Buehler's original equation. | |
| Butyric acid | 0-130° | 3'14 | -1'316 | 1'05 | -2'326 | 1'95 | 5'2 | 53'3 | |
| <i>n</i> -Propyl alcohol | 0-90 | 3'75 | -1'658 | 1'89 | -4'020 | 1'0 | 4'9 | 78'6 | |
| Ethyl acetate | 0-70 | 4'20 | -1'693 | 1'18 | -2'767 | 1'23 | 1'3 | 15'7 | |
| Ethylene chloride | 0-80 | 3'31 | -1'279 | 0'95 | -2'280 | 1'0 | 0'4 | 11'1 | |
| Chloroform | 0-60 | 3'22 | -1'238 | 0'86 | -2'078 | 1'6 | 2'0 | 13'3 | |
| Chlorobenzene | 20-160 | 4'18 | -1'610 | 1'00 | -2'464 | 1'7 | 3'2 | 1'0 | |
| Carbon tetrachloride | 20-170 | 3'30 | -1'400 | 0'87 | -1'996 | 2'0 | 5'0 | 63'2 | |
| Toluene | 0-110 | 4'93 | -1'966 | 1'13 | -2'730 | 1'3 | 3'9 | 4'7 | |
| Acetone | -87-56 | 5'17 | -2'052 | 1'30 | -3'140 | 1'9 | 3'0 | 4'5 | |
| Methyl alcohol | -87-0 | 2'54 | -1'045 | 1'70 | -3'814 | 1'1 | 6'2 | 46'2 | |
| Ether | -95-0 | 4'77 | -1'942 | 1'36 | -3'180 | 2'0 | 1'3 | 18'6 | |
| Bromobenzene | 60-143 | 3'34 | -1'264 | 0'75 | -1'860 | 1'0 | 4'0 | 9'7 | |
| Ethylformate | 0-50 | 4'85 | -1'955 | 1'24 | -2'962 | 0'7 | 1'0 | 6'8 | |
| <i>iso</i> Butyl bromide | 0-90 | 3'64 | -1'469 | 1'00 | -2'337 | 1'4 | 1'1 | 27'2 | |
| Methyl <i>isobutyrate</i> | 0-90 | 4'87 | -2'027 | 1'34 | -3'082 | 2'0 | 2'4 | 20'6 | |
| <i>o</i> -Nitrotoluene | 0-100 | 3'88 | -1'492 | 1'61 | -3'937 | 1'2 | 0'7 | 4'3 | |
| Ethyl iodide | 0-70 | 4'00 | -1'572 | 0'94 | -2'265 | 0'5 | 2'9 | 9'1 | |
| Methyl ethyl ketone | 0-80 | 4'77 | -1'930 | 1'22 | -2'895 | 1'1 | 0'9 | 9'0 | |
| <i>m</i> -Toluidine | 0-60 | 4'40 | -1'744 | 2'50 | -6'010 | 0'9 | 1'7 | 24'2 | |
| Octane | 0-80 | 3'85 | -1'602 | 1'12 | -2'552 | 0'6 | 0'7 | 7'0 | |
| <i>m</i> -Xylene | 0-130 | 4'30 | -1'694 | 1'18 | -2'840 | 1'1 | 4'0 | 8'8 | |
| Nitrobenzene | 5-80 | 4'76 | -1'810 | 1'72 | -4'285 | 0'7 | 1'0 | 12'0 | |
| Propyl acetate | 0-100 | 4'00 | -1'639 | 1'20 | -2'760 | 1'2 | 1'1 | 27'0 | |
| Ethyl alcohol | -98-70 | 2'98 | -1'285 | 1'50 | -3'200 | 2'2 | 15'9 | 72'5 | |
| Acetic acid | 20-110 | 3'34 | -1'375 | 1'03 | -2'336 | 0'9 | 1'0 | 37'8 | |

The original Buehler's equation has general constants as will be evident from the equation itself.

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TABLE III.

| Temp. | γ obs. | γ Calc. | | % Difference. | |
|---|---------------|---------------------|------------------------------|--------------------|------------------------------|
| | | Buehler's equation. | Buehler's modified equation. | Buehler's equation | Buehler's modified equation. |
| Propionic acid : ($m=0.955$; $C=-2.16$). | | | | | |
| 0° | 28.80 | 37.64 | 29.20 | 30.4 | 1.39 |
| 10 | 27.50 | 36.28 | 28.03 | 31.9 | 1.92 |
| 20 | 26.50 | 34.93 | 26.94 | 31.8 | 1.66 |
| 30 | 25.60 | 33.73 | 25.76 | 31.7 | 0.62 |
| 40 | 24.60 | 32.56 | 24.59 | 32.4 | -0.04 |
| 50 | 23.65 | 31.49 | 23.50 | 33.0 | -0.60 |
| 60 | 22.60 | 30.45 | 22.48 | 34.7 | -0.53 |
| 70 | 21.70 | 29.38 | 21.40 | 35.4 | -1.38 |
| 80 | 20.70 | 28.39 | 20.41 | 37.2 | -1.40 |
| 90 | 19.80 | 27.39 | 19.45 | 38.4 | -1.76 |
| 100 | 18.75 | 26.41 | 18.52 | 40.5 | -1.22 |
| 110 | 17.80 | 25.45 | 17.60 | 43.0 | -1.12 |
| 120 | 16.80 | 24.50 | 16.71 | 45.7 | -0.53 |
| 130 | 15.80 | 23.55 | 15.83 | 49.0 | 0.19 |
| 140 | 14.90 | 22.55 | 14.82 | 51.4 | -0.53 |
| Benzene : ($m=1.22$; $C=-2.9167$). | | | | | |
| 0 | 31.87 | 33.24 | 31.87 | 4.30 | 0.0 |
| 10 | 30.19 | 31.89 | 30.19 | 5.63 | 0.0 |
| 20 | 28.88 | 30.20 | 28.88 | 4.57 | 0.0 |
| 30 | 27.58 | 28.67 | 27.56 | 3.96 | -0.07 |
| 40 | 26.28 | 27.30 | 26.24 | 3.89 | -0.15 |
| 50 | 25.09 | 26.83 | 25.02 | 6.93 | -0.30 |
| 60 | 23.82 | 24.82 | 23.81 | 4.22 | -0.04 |
| 70 | 22.55 | 23.60 | 22.57 | 4.67 | -0.09 |
| 80 | 20.28 | 22.75 | 20.36 | 12.15 | 0.39 |
| *100 | 18.02 | 19.57 | 18.13 | 8.60 | 0.61 |

* This temperature is above B. P.

If the assumption that $I/P=1.2$ is done away with and Buehler's equation is written in the form $\log \log \eta = m\gamma^{\frac{1}{4}} + c$ (which will henceforward be referred to as Buehler's modified equation) it is found that the equation gives very satisfactory results, and surprisingly enough, by some compensation of errors, the equation is found to apply satisfactorily not only to simple but also to associated liquids, not only to ordinary temperatures but also to temperatures above the boiling point of liquids.

Table II gives a comparison of the three equations.

In order to show the extent to which the Buehler's modified equation agrees with actual measurements, the results for propionic acid, an associated liquid, and for benzene, a simple liquid, are given in detail in Table III.

A number of other equations connecting viscosity with density with or without temperature can be combined with Sugden's parachor equation and the equations so obtained giving relationships between viscosity and surface tension are found, on examination, to be quite accurate though none of them is as simple as the modified Buehler's equation.

The data have been taken from Landolt Bornstein Tabellen (1923 edition) and Tables Annuelles (Vol. V, 1937).

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DILATOMETRIC STUDIES ON SUPERSATURATION. PART I.

By A. C. CHATTERJI AND RAMA GOPAL.

It has been confirmed that no sudden change in volume occurs at the saturation temperature when a solution is cooled from unsaturated to the supersaturated state in the cases of solutions of potassium nitrate, sodium nitrate, potassium sulphate, sodium acetate and oxalic acid in water. It has been demonstrated that inflexions in temperature-volume curves of any cooling solution occur only when crystallisation takes place, either automatically, or is induced artificially by inoculation. An attempt has also been made to show that no sudden changes which can be exhibited as changes in volume of a cooling solution occur in the molecular state at the lower limit of the metastable range *i.e.*, at the labile temperature.

It has been shown by various workers that the physical properties *e.g.*, conductivity (Heim, *Ann. Physik*, 1886, *iii*, 27, 673), specific viscosity (Nichol, *J. Chem. Soc.*, 1887, 51, 389; Taimini, *J. Phys. Chem.*, 1928, 32, 604), specific gravity, specific heat, heat of solution (Bindel, *Ann. Phys. Chem.*, 1890, *iii*, 40, 370) and density (Scott and Badger, *J. Phys. Chem.*, 1936, 40, 461) of supersaturated solutions do not suffer any abrupt change either at the saturation temperature or at any other point below this temperature to which it has been possible to cool the solution before spontaneous crystallisation sets in.

The works of Miers and Issac (*J. Chem. Soc.*, 1906, 89, 413) appear to show, however, that a change in solution occurs at the metastable temperature. The experiments carried out by Nayar (*Proc. Acad. Sci., U.P.*, 1931, 1, 100) on dilatation of supersaturated solutions seem to corroborate the conclusions of Miers and Issac and further claim to establish a break at the saturation point. But experiments of Hook (*J. Phys. Chem.*, 1937, 41, 593) point out that temperature-volume curves of a number of solutions "show no non-uniformity at the saturation point." As experiments of Hook are in general agreement with the hypothesis that the physical properties do not suffer any discontinuity at the saturation temperature, the experimental results obtained in the preliminary investigations of Nayar pointing out such a break require further investigation.

Oxalic Acid Solution.

Aqueous solutions of different substances, saturated at temperatures varying from 50° to 70°, were put successively into a dilatometer similar to that of Nayar (*loc. cit.*) after filtering so as to remove dust particles,

that might be present in the salts. Solutions were immediately covered with a layer of paraffin oil in order to prevent any evaporation which might alter the saturation temperature of the solution. The bulb of the dilatometer was dipped in a big beaker containing water. Further the beaker was covered with cotton pads with a little opening left for taking observations. This device was adopted to ensure a slow cooling. The solution was then heated to a temperature approximately 10° higher than the saturation point and the apparatus was completely fitted up as was done by Nayar and Hook. Then the beaker was allowed to cool slowly. Changes in volume were read on the capillary tube fitted on a metre scale. The rate of cooling was controlled by a micro-burner put under the beaker.

In the table given below, scale readings are recorded along with the corresponding time and temperature for the oxalic acid solution.

TABLE I.

Oxalic acid solution.

| Time. | Temp. | Scale readings. | Time. | Temp. | Scale readings. |
|--------|----------|-----------------|---------|-----------|-----------------|
| 0 min. | 76° | 99·0 | 76 min. | 58° C.T.* | 26·0 |
| — | 74 | 92·2 | 80 | 58·4 | 18·0 |
| 14 | 72 | 85·3 | — | 58·5 | 15·0 |
| 22 | 70 | 77·5 | — | 58·8 | 10·0 |
| 30 | 68 S.T.* | 69·2 | — | 59·0 | 6·0 |
| 40 | 66 | 60·3 | — | 58·5 | 4·0 |
| 49 | 64 | 51·6 | 86 | 58·3 | 3·0 |
| 59 | 62 | 43·0 | 90 | 58·0 | 0·0 |
| 65 | 60 | 34·0 | 97 | 57·3 | -3·0 |

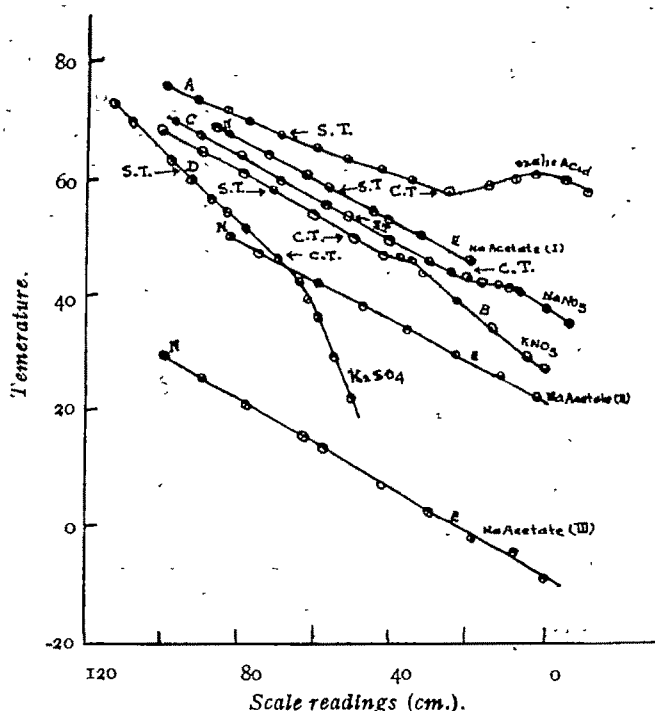
From the above table the temperature-volume curve for oxalic acid was drawn as shown in Fig. 1, curve A. In all other cases similar readings were obtained and graphs B, C, D and E were drawn and are given in Fig. 1.

From the curves given in Fig. 1 it is apparent that the graphs can be divided into two different types. The first type contains an inflexion while the second type is without it. In all these cases, however, one thing

* S.T. denotes the saturation temperature and C.T. the temperature at which crystallisation is observed to start.

is common *i.e.*, no discontinuity occurs at the point where the solutions pass from the unsaturated into the supersaturated or metastable state. In every case in which spontaneous crystallisation occurs (curves A, B, C and D) there is a change in the direction of the curve at the point where crystalli-

Fig. I.



sation begins with a consequent release of supersaturation at a little lower temperature. The magnitude and shape of the inflexion depend upon the quantity of heat evolved and the amount of the crystals formed on the release of supersaturation. In the second type (curve E) *i.e.*, in the case of sodium acetate, which is capable of remaining in the supersaturated condition to a great extent, no crystallisation took place even when -8° was reached, the saturation temperature being 58° . It is clear therefore that sodium acetate does not crystallise within the limits of the temperatures tried and no break in the curve is noticed.

From the curves it can also be seen that inflexion is well marked in the case of oxalic acid, not so clear in the case of potassium sulphate and does not occur at all in the case of sodium acetate. This is due to

the fact that comparatively large amount of crystals is released in the case of oxalic acid, temperature coefficient of solubility being 2.7 g. per degree, whereas in the case of potassium sulphate, etc., quantity released is small, the temperature coefficient of solubility being 0.2 g. per degree.

It is therefore clear that the inflexion in temperature-volume curve at the saturation temperature observed by Nayar is merely due to crystallisation that sets in at that point and that it is not a characteristic of the saturation temperature itself. This is to say there occurs no sudden change in the volume of a solution as it passes from the unsaturated into the supersaturated state indicating no sudden change in the state of the entities concerned at the saturation temperature. Continuing the same trend of reasoning, there is no reason to suppose that a sudden change in the volume should occur at the lower limit of the metastable range (*i.e.*, at the labile temperature) unless of course crystallisation sets in. For example, in the case of sodium chlorate solution crystallisation does not occur even at the labile temperature (Miers, *loc. cit.*). Even moderate shaking has no effect and the solution passes far into the labile region without crystallising. A similar case is noticed in sodium acetate solution although no supersolubility data is available in the literature. If, therefore, we bring about crystallisation in these cases by inoculation, curves similar to that of oxalic acid should be obtained. Conversely, if crystallisation in oxalic acid be stopped somehow, the inflexions observed should disappear or at least shifted to some lower temperature where crystallisation may set in. With a view to get further information on this point experiments given below were carried out.

Oxalic Acid Solution with Inoculation.

Oxalic acid solutions to which varying amounts of gelatine were added crystallised at the same temperature as pure oxalic acid solution indicating no effect of added gelatine.

The next procedure suggested above, *i.e.* to induce crystallisation by inoculation in sodium acetate and sodium chlorate solutions was therefore adopted. Sodium chlorate solution, however, began to crystallise at the saturation temperature in presence of oil. But sodium acetate solution gave very satisfactory results, hence it was utilised in the following set of experiments.

The simple dilatation apparatus used in the previous experiments is modified so as to enable one to inoculate the cooling solution with a minute crystal of the substance without disturbing the rest of the apparatus, at

any desired temperature. It carries an upright side-tube of approximately the same height as the neck of the dilatometer. At the upper end of the tube an arrangement is made to enable one to drop a germ crystal into the solution by slightly twisting the handle of the crystal-carrying cup as is the case in the vapour density apparatus of Victor Meyer. The whole arrangement is made air-tight. The temperature readings are taken as before and the graphs given in Figs. 2 and 3 below are obtained from them.

FIG. 2

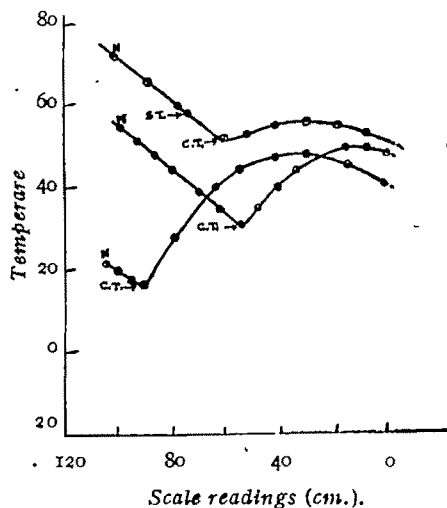
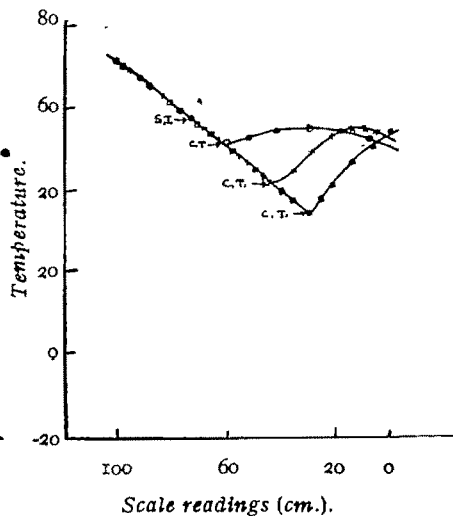


FIG. 3



In order to investigate a wide range of temperatures with the same capillary tubing the following device is adopted in the cases represented by the curves E of Fig. 1 and by those of Fig. 2. "No readings are taken until the solution cools down to the temperature marked by the letter N on the curves of these figures. At this temperature recording is started. The scale reading at this temperature is brought to 100 cm. approximately in every case. This is done by attaching a bent capillary tubing filled with oil to the main capillary tube and dipping the end of the bent tube in a beaker containing oil. It is disconnected when the solution cools down to the required temperature." In Fig. 3 the initial reading for every curve is 100 cm. and 72°. Inoculation in Fig. 2 are made at 52°, 31° and 16°; while in Fig. 3 at 52°, 42°, and 35°. The straight portions of the curves in Fig. 3 are almost coincident except a little deviation due to the experimental errors.

From these series of graphs it is clear that a crystallisation process is always accompanied by an inflexion in the curve. But the curves E in Fig. 1 show that if there is no crystallisation there is no inflexion. The graphs of Figs. 2 and 3 are of the type of oxalic acid. Hence these experiments conclusively prove that inflexions can be produced at any desired temperature within the supersaturated region by bringing about crystallisation at that temperature artificially by inoculation. If we suppose that the labile temperature for sodium acetate solution studied here is included within this wide region of supersaturation (from 58° to -8°), and this seems to be fairly certain as the solution sets to solid mass immediately on inoculation, it can be said with a fair degree of accuracy that no inflexion occurs even at the lower limit of the metastable range, *i.e.*, at the labile temperature of Miers.

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AN ATTEMPT TO CORRELATE THE CONSTITUTION OF GLASS WITH THE POTENTIAL AT GLASS- ELECTROLYTE INTERFACES.

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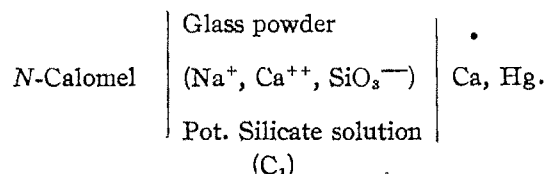
The E. M. F. of cells in which powdered glass in contact with potassium silicate solutions of different concentrations formed one component was measured, the other components being normal calomel and calcium-amalgam electrodes. Powdered glass has been found to behave as a sparingly soluble salt. An attempt has been made to correlate the results obtained with the constitution of glass.

If glass be considered a definite compound, a saturated solution of powdered soft glass in water will furnish definite amounts of sodium, calcium and silicate ions and will conform to a definite solubility product value. If now a solution of potassium silicate be in contact with powdered glass and be saturated with it, an equilibrium will be set up among the sodium, calcium and silicate ions, for the concentrations of which the law of mass action will apply. The bulk of the silicate and the concentrations of the cations will be controlled by the concentration of the silicate ion through the solubility product of glass. The system is thus comparable with a solution of potassium chloride in contact with mercurous chloride and saturated with it, the concentrations of the cations in both the cases being controlled through variations in the concentrations of the anions. It would thus be possible to set up an electrode of the second type if one of the cation metals of glass be put in contact with a solution of potassium silicate in contact with powdered glass and saturated with it. Owing, however, to the unstable nature of the cation metals of glass, amalgam electrodes will have to be used.

In the present experiments a cell has been set up on the above principle, and the variations in the E. M. F. of the cell for different concentrations of the potassium silicate solution have been measured. On the basis of certain assumptions, it is possible to derive an expression which connects the E. M. F. of the cell with the constitution of glass. This expression has been applied to the experimental values to get information about the possible constitution of glass considered as a compound.

Derivation of the Expression for the E. M. F.

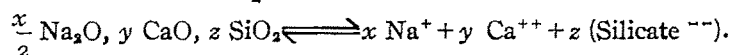
Considering the cell,



the E. M. F. of the cell is given by the expression

$$e_1 = E_{\text{Calomel}} - \left\{ E^\circ_{\text{Ca}^{++}} + \frac{RT}{nF} \log [\text{Ca}^{++}] \right\} \quad \dots (i)$$

where $E^\circ_{\text{Ca}^{++}}$ represents the normal potential of calcium ions. Let the glass have a composition, $\frac{x}{2} \text{Na}_2\text{O}$, $y \text{CaO}$, $z \text{SiO}_2$. On ionisation we get



By applying the law of mass action we get:

$$[\text{Na}^+]^x [\text{Ca}^{++}]^y [\text{Silicate}^{--}]^z = K$$

$$\text{or} \quad [\text{Na}^+]^x [\text{Ca}^{++}]^y = \frac{K}{[\text{Silicate}^{--}]^z} \quad \dots (ii)$$

Let $\frac{x}{y} = p$, i.e., for every calcium ion furnished by the ionisation of the glass in a saturated solution, let p -ions of sodium be obtained. Thus in a saturated solution of glass,

$$[\text{Na}^+] = p [\text{Ca}^{++}].$$

Substituting this value in equation (ii) we get,

$$p^x \cdot [\text{Ca}^{++}]^x \cdot [\text{Ca}^{++}]^y = \frac{K}{[\text{Silicate}^{--}]^z}$$

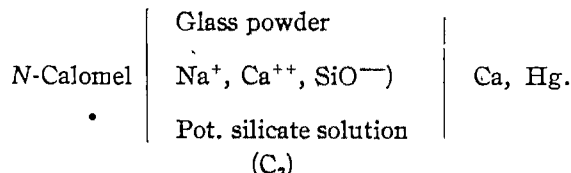
$$\text{or} \quad [\text{Ca}^{++}] = \left\{ \frac{K}{p^x} \cdot \frac{1}{[\text{Silicate}^{--}]^z} \right\}^{\frac{1}{(x+y)}}$$

Substituting this value for the calcium ion concentration in equation (i) we get

$$e_1 = E_{\text{Calomel}} - \left\{ E^\circ_{\text{Ca}^{++}} + \frac{RT}{nF} \cdot \frac{1}{(x+y)} \cdot \log \left(\frac{K}{p^x} \cdot \frac{1}{[\text{Silicate}^{--}]^z} \right) \right\}$$

$$\text{or } e_1 = E_{\text{Calomel}} - E^\circ_{\text{Ca}^{++}} - \frac{1}{(x+y)} \cdot \frac{RT}{nF} \log \frac{K}{p^x} + \frac{z}{(x+y)} \cdot \frac{RT}{nF} \log [\text{Silicate}^{--}]_{C_1}.$$

Next consider an exactly similar cell but with a different concentration of potassium silicate solution = C_2 . viz.,



As before the E. M. F. of this cell will be given by

$$e_2 = E_{\text{Calomel}} - E^{\circ}_{\text{Ca}^{++}} - \frac{1}{(x+y)} \cdot \frac{RT}{nF} \log \frac{K}{p^{\#}} + \frac{z}{(x+y)} \cdot \frac{RT}{nF} \log [\text{Silicate}^{--}]_{C_2}.$$

Therefore,

$$e_1 - e_2 = \frac{z}{(x+y)} \cdot \frac{RT}{nF} \cdot \left\{ \log [\text{silicate ion}]_{C_1} - \log [\text{silicate ion}]_{C_2} \right\}.$$

$$\text{or} \quad e_1 - e_2 = \frac{z}{(x+y)} \cdot \frac{RT}{nF} \cdot \log \frac{[\text{silicate ion}]_{C_1}}{[\text{silicate ion}]_{C_2}} \quad \dots \quad (iii)$$

The above expression has been applied to the present experiments.

E X P E R I M E N T A L.

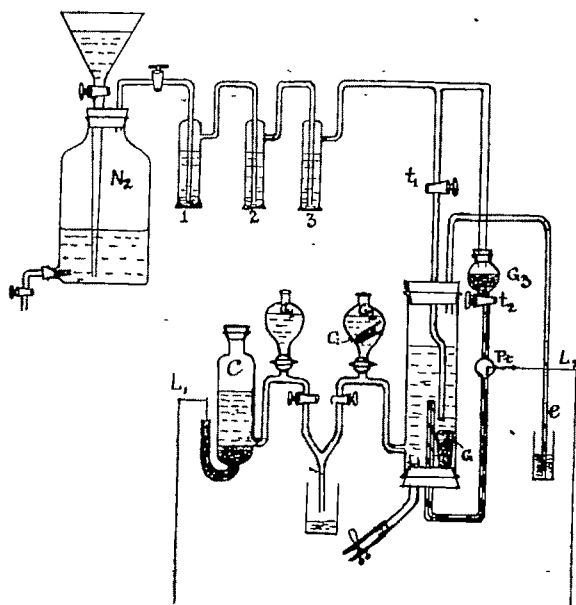
A sample of glass was prepared by fusing together sodium carbonate, lime and silica. Pure anhydrous sodium carbonate (40 g.), dry calcium carbonate (11 g.) and washed precipitated silica (75 g.) were intimately mixed together. The mixture was charged into fire-clay crucibles and heated for 3-4 hours in an electric furnace which gave a temperature of about 1000-1100°. The resulting sample of glass was finely powdered and stocked for use during subsequent experiments.

The exact composition of the above sample of glass was determined by analysis which gave the following percentage values (Na₂O, 21.8; CaO, 6.0; SiO₂, 72.2) corresponding approximately to an analytical composition, 3Na₂O. CaO. 10 SiO₂.

The calcium amalgam used during the measurements was prepared by the method recommended by Neuhausen (*J. Amer. Chem. Soc.*, 1922, **44**, 1445). Sufficient quantity of pure mercury was placed in a flat-bottomed glass basin so as to just cover up the bottom of the vessel. A large cathode surface without using too much mercury is desirable. A 1.75M solution of calcium chloride was poured over the mercury to form a layer about 2 cm. high. A perforated circular disc of platinum of 15 sq. cm. surface area served as the anode. The anode was adjusted at the proper height and the electrolysis was carried out with a current of 3.5 amps. After the amalgam had been formed, the solution was drained off, the surface of the amalgam was wiped with a dry filter paper, and it was then quickly transferred to a stoppered vessel and preserved in an atmosphere of nitrogen.

Neuhausen has recommended an atmosphere of carbon dioxide for preserving the amalgam. In the present experiments an inert atmosphere of nitrogen has been found more suitable as carbon dioxide cannot be used where measurements with alkali silica solutions are concerned.

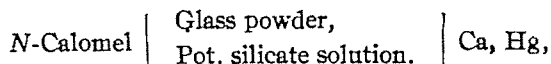
FIG. 1.



The experimental arrangement for the cell is based on the apparatus recommended by Fosbinder (*J. Amer. Chem. Soc.*, 1929, **51**, 1349). Certain necessary modifications have been introduced. The arrangement is shown diagrammatically in Fig. 1. Nitrogen from a six litre aspirator bottle was allowed to stream through a series of bubblers (1, 2, 3) containing concentrated ferrous sulphate solution and alkaline pyrogallol. With the help of the taps t_1 and t_2 , the nitrogen could bubble directly into the solution in the experimental tube or through G_3 and the capillary tube, as desired. Potassium silicate solution of requisite concentration was thoroughly shaken up with the powdered glass and filled into the experimental tube. The same solution was also put in the globe G_2 . The vessels marked G contained solid powdered glass and served to maintain the solution saturated with respect to glass. The amalgam was contained in the globe G_3 and was allowed to enter the solution in the experimental tube through the capillary. During its passage the amalgam swept over the platinum wire (Pt) which served as the terminal at the amalgam end of the cell. C was a normal calomel electrode. By regulating the flow of liquids from G_1 and G_2 , the junction was constantly renewed and the junction potential was

considerably minimised. The potential was measured through the leads L_1 and L_2 , by means of a Tinsley potentiometer.

The cell set up was



and the E. M. F. with potassium silicate solutions of different concentrations were measured. The potassium silicate used was a sample of Kahlbaum's metasilicate. The average E. M. F. values of several runs are given in the following tables.

It should be mentioned that considerable difficulty was encountered in protecting the amalgam and stopping it from choking the capillary. The difficulty, however, was overcome to a large extent by maintaining a slight regulated pressure of nitrogen through the globe G_3 . With each concentration of potassium silicate solution, a large number of E. M. F. readings were taken and only those values which agreed closely within a few millivolts have been utilised.

Freezing points of potassium silicate solutions have been determined by Kahlenburg and Lincoln (*J. Phys. Chem.*, 1898, 2, 77). Attempts were made to determine the activity coefficients of potassium silicate solutions from these data by using the Lewis and Linhart formula (*J. Amer. Chem. Soc.*, 1919, 41, 1952). Owing, however, to the doubtful nature of the value of ν , the number of ions furnished on dissociation, the results were not satisfactory. An accurate series of conductivity measurements of sodium silicate solutions have been made by Harman (*J. Phys. Chem.*, 1925, 29, 1155). These data have been used to calculate the degree of dissociation of potassium silicate solutions, the values for the sodium and potassium salts being taken as comparable. The degrees of dissociation reckoned in the above manner are given in Table I. In Table II are given the values of

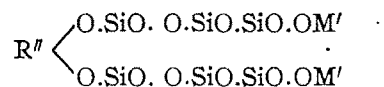
$(e_1 - e_2)$ and the corresponding values of $\left(\frac{z}{x+y}\right)$ as calculated with the help of equation (iii).

| TABLE I. | | | TABLE II. | | |
|---------------------|---|---------------------------|------------------------|-------------|-----------------|
| Pot. silicate soln. | $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ | [Silicate ⁻⁻] | Cell. | $e_1 - e_2$ | $\frac{z}{x+y}$ |
| 1.00 N | 0.5 | 0.5 | $e_N - e_{0.1N}$ | 0.043 volt. | 1.79 |
| 0.10 | 0.812 | 0.081 | $e_N - e_{0.02N}$ | 0.027 | 2.18 |
| 0.04 | 0.91 | 0.036 | $e_N - e_{0.01N}$ | 0.082 | 1.19 |
| 0.02 | 0.95 | 0.019 | $e_{0.1N} - e_{0.02N}$ | 0.032 | 1.76 |
| 0.01 | 0.97 | 0.0097 | $e_{0.1N} - e_{0.01N}$ | 0.061 | 2.20 |

DISCUSSION.

The experimental results show that powdered glass behaves as a sparingly soluble salt. When glass is dissolved in water, it furnishes calcium ions which can function to a large extent as reversible ions in an electrode process. Those facts support the view that pure glass is a true chemical compound.

A considerable difference of opinion exists as to the chemical composition of glasses, which are generally regarded as a complex mixture of several simple silicates or a solid solution. The results of a study of durability of soda-lime-silica glasses towards chemical reagents led some investigators to postulate the existence of a compound, $6\text{SiO}_2 \cdot \text{CaO} \cdot \text{Na}_2\text{O}$. The work of Foerster (*Z. anal. Chem.*, 1894, **35**, 381) on the action of water on vessels of various kinds of glasses showed that minimum corrosion occurred with the glass of approximately the $6\text{SiO}_2 \cdot \text{R}'' \text{O} \cdot \text{M}'_2\text{O}$ composition. This particular composition has frequently been referred to in literature as the "normal glass". From the results of analyses of a large number of glasses and Foerster's experiments, Zulkowski (*Chem. Ind.*, 1899, **22**, 280) came to the conclusion that there must be a definite complex silicate in glass of composition stated above, and ascribed to it the formula,



A complex compound of the composition, $6\text{SiO}_2 \cdot \text{CaO} \cdot \text{Na}_2\text{O}$, will give both sodium and calcium ions in solution, and, when the complex is broken down, the ratio of silica ions (z) to the sum of calcium (x) and sodium (y) ions will be equal to 2. The results in Table II show that the ratio $z : (x + y)$ is fairly constant, and the average value of the ratio is 2:1. It is not likely that the ratio will have the same value in all cases if glass were a mixture of simple silicates.

Further experiments with sodium amalgam and an improved method for elimination of liquid junction are being attempted.

NEW COMPOUNDS OF GALLIUM. PART IV. GALLIUM HYDROXYL AMMONIUM ALUM AND DOUBLE SULPHATES OF GALLIUM AND PRIMARY, SECONDARY AND TERTIARY ALIPHATIC AMINES.

BY PANCHANAN NEOGI AND KANAI LAL MONDAL.

Gallium sulphate has been combined with hydroxylamine sulphate and sulphates of primary, secondary and tertiary aliphatic amines. Hydroxylamine has yielded an alum crystallising from water with 24 molecules of water. The double sulphates containing amine sulphates contain less than 24 molecules of water, some containing 16 and others 18 molecules. Double sulphates of two primary, one secondary and two tertiary amines have been obtained.

Soret (*Arch. Phys. nat.*, 1888, **20**, 528) prepared gallium ammonium alum by combining gallium sulphate and ammonium sulphate. In this paper, gallium sulphate has been combined with hydroxylamine sulphate and sulphates of primary, secondary and tertiary aliphatic amines. Hydroxylamine has yielded with gallium sulphate an alum crystallising from water with 24 molecules of water. The double sulphates containing amine sulphates contain less than 24 molecules of water of crystallisation. Double sulphates of two primary, one secondary and two tertiary amines have been obtained.

EXPERIMENTAL.

Gallium Hydroxyl-Ammonium alum.—Equimolecular quantities of gallium sulphate and hydroxylamine sulphate were mixed together in aqueous solutions and then evaporated in a vacuum desiccator. The solid obtained was dissolved in the least quantity of water and the double sulphate precipitated by means of absolute alcohol. It was crystallised several times from water. Crystals were large and found, after drying for two days in air, to contain 24 molecules of water. It effloresces when kept exposed to the air for a long time. It is insoluble in alcohol. [Found: N, 2.95; Ga, 13.84; SO₄, 37.12. NH₂(OH)₂·H₂SO₄, Ga₂(SO₄)₃, 24H₂O requires N, 2.73; Ga, 13.67; SO₄, 37.5 per cent].

Gallium isoAmylammonium Sulphate.—To a molecule of gallium sulphate dissolved in water, an aqueous solution of a little more than a molecule of isoamylamine sulphate was added. The mixture was allowed to evaporate in a vacuum desiccator over sulphuric acid till a dry solid was obtained. It was treated with absolute alcohol and the free amine sulphate, which is soluble in alcohol, was removed by filtration. The residue was dissolved in the smallest quantity of water and the double sulphate precipitated by the addition of absolute alcohol. It was crystallised from water

and analysed after drying in air. The double sulphate is soluble in water but insoluble in alcohol, ether and other common organic solvents. On keeping, it gradually became insoluble in water. It melts with decomposition at a high temperature. [Found: N, 2.7; Ga, 14.52; SO₄, 38.48. (C₆H₁₁NH₂)₂. H₂SO₄. Ga₂(SO₄)₃. 16H₂O requires N, 2.83; Ga, 14.17; SO₄, 38.86 per cent].

Gallium isoButylammonium Sulphate.—The double sulphate was prepared in the same way as the above compound. In properties it is similar to that compound. [Found: N, 2.75; Ga, 14.91; SO₄, 40.22. (C₄H₉NH₂)₂. H₂SO₄. Ga₂(SO₄)₃. 16H₂O requires N, 2.91; Ga, 14.58; SO₄, 40 per cent].

Gallium Diethylammonium Sulphate.—An aqueous solution of a molecule of diethylamine sulphate was mixed with a little more than a molecule of gallium sulphate dissolved in water and the mixed solution was evaporated in a vacuum desiccator over sulphuric acid. The solid obtained was treated with absolute alcohol. The double sulphate being soluble in alcohol went into solution. It was separated by filtration from gallium sulphate which is insoluble in absolute alcohol. The filtrate on evaporation gave deliquescent crystals of the double sulphate which was crystallised from water before analysis. It is very soluble in water but insoluble in acetone, ether, chloroform etc. This double sulphate also melts with decomposition at a high temperature. [Found: N, 2.97; Ga, 14.46; SO₄, 38.80. {(C₂H₅)₂NH} . 2H₂SO₄. Ga₂(SO₄)₃. 18H₂O requires N, 2.81; Ga, 14.05; SO₄, 38.55 per cent].

Gallium Tri-isoamylammonium Sulphate.—A molecule of gallium sulphate dissolved in water was mixed with a little more than a molecule of tri-isoamylamine sulphate and allowed to evaporate in vacuum over sulphuric acid. The dry sulphate was treated with absolute alcohol to remove the free amine sulphate and then crystallised twice from water. The compound was analysed after drying between the folds of filter papers. It decomposes on keeping and becomes insoluble in water. [Found: N, 2.19; Ga, 10.68; SO₄, 29.81. {C₅H₁₁}₃N} . 2H₂SO₄. Ga₂(SO₄)₃. 16H₂O requires N, 2.20; Ga, 11.02; SO₄, 30.28 per cent].

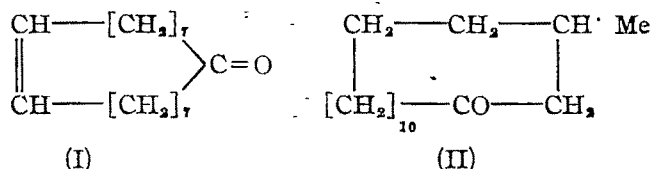
Gallium trimethylammonium sulphate was obtained in the same way as the tri-isoamylammonium sulphate. It is very soluble in water. [Found: N, 3.35; Ga, 14.92; SO₄, 39.28. {(CH₃)₃N} . 2H₂SO₄. Ga₂(SO₄)₃. 18H₂O requires N, 2.89; Ga, 14.46; SO₄, 39.67 per cent].

STUDIES IN LONG-CHAIN ACIDS. PART IV.

BY P. C. MITTER AND BIDYUT KAMAL BHATTACHARYYA.

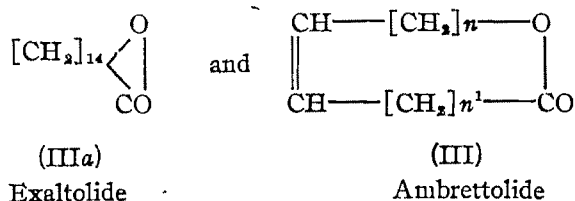
Aleuritic acid, isolated from shellac, has been converted into epi-ambrettolic acid and epi-ambrettolide as well as ethyl 16-cyano- Δ^9 -hexadecenoate and homocivetonic acid.

Since the elucidation of the constitution of civetone (I) and muscone (II) as a result of the classical researches of Ruzicka, the study of the multimembered ring systems has acquired a new importance



According to Luttringhaus and Ziegler (*Annalen*, 1937, **528**, 181) the odour depends primarily on the size of the ring, the only condition being the presence of a place of disturbance (Störungstelle) on the molecule. The nature of the 'place of disturbance' may differ widely in chemical character in being either a ketone, a lactone, an anhydride, ester, acetal or even an endocyclic imino grouping, without materially influencing the character of the odour. Polymethylene rings with fifteen to seventeen members and including one of these functional groups show throughout the odour of musk or of ambergris. With lower membered rings (C_{14}) the odour resembles cedar wood, while with still lower members the odour becomes camphoraceous.

Kerschbaum (*Ber.*, 1927, **60**, 902) has shown the presence of the lactone of ω -hydroxypentadecic acid (IIIa) and the lactone of ω -hydroxy- Δ^9 -hexadecic acid (III; $n=8$; $n^1=5$), ambrettolide in angelica root oil and in ambretto seed oil, the vegetable oils possessing odour of musk.

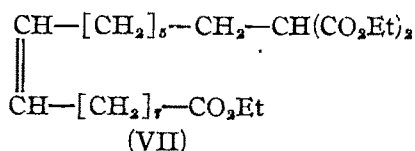
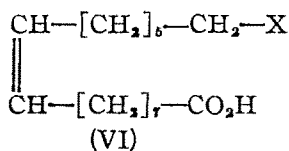
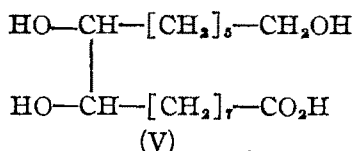
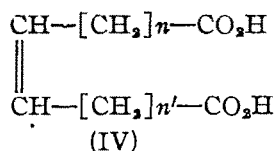


Whereas muscone is a saturated compound, civetone contains one double bond in the molecule, but the presence of the double bond has nothing to do

with the odour of the compound which has been found by Ruzicka to remain unchanged on saturation. A similar observation has been made by Kerschbaum (*loc. cit.*) with ambrettolide (III), where the saturation of the double bond does not alter the odour.

While *dl*-muscone has been synthesised by Ziegler and Weber (*Annalen*, 1934, 512, 164), and also by Ruzicka and Stoll (*Helv. Chim. Acta*, 1934, 17, 1308), the synthesis of civetone has not yet been accomplished. The chief reason for this is that the corresponding acid, namely Δ^9 -hexadecene-1:16-dicarboxylic acid (IV, $n=n'=7$) which should give this ketone on cyclisation can not be obtained with known synthetic methods. Ruzicka (*Helv. Chim. Acta*, 1932, 15, 1459) has, however, prepared a lower homologue of civetone by the distillation of the yttrium salt of Δ^8 -pentadecene-1:15-dicarboxylic acid (IV, $n=6$; $n'=7$) which he named civetic acid.

It has now been possible to develop a new method for the synthesis of the unsaturated acids of the type mentioned before, starting from aleuritic acid (V) which can be obtained by the alkaline hydrolysis of shellac. A glance at the formula of aleuritic acid (V) and civetone (I) would show little relationship, but when it is considered that it is possible to convert aleuritic acid to a ω -halogenated Δ^9 -hexadecenoic acid (VI, X=Halogen), it becomes at once clear that both civetic (IV, $n=6$; $n'=7$) and homocivetic acids (IV, $n'=n=7$) are synthesisable from it through the usual operations.



Considerable difficulties were encountered in the conversion of aleuritic acid into the desired halogenated acid (VI). When an ether suspension of aleuritic acid is treated with a solution of phosphorus di-iodide, ω -iodo- Δ^9 -hexadecenoic acid (VI, X=I) is obtained. This method of double-bond formation has been extensively used by Kuhn and Winterstein (*Helv. Chim. Acta*, 1928, 11, 87; *cf.* Kuhn, *J. Chem. Soc.*, 1938, 605) in the synthesis of polyenes.

The ω -iodo acid could not be purified. Its silver salt on being heated in xylene undergoes lactonisation, giving a seventeen-membered lactone (III, $n=6$; $n'=7$), which has been named epi-ambrettolide.

It is found to possess a musk-like odour but more fresh and floral as is commonly the case with lactones (*cf.* Kerschbaum, *loc. cit.*).

The corresponding hydroxy acid namely epi-ambrettolic acid (VI, $X=OH$) has been obtained in an impure state by acidification of the alkaline washings of the lactone. The acid could not be purified. Attempts to obtain the pure acid by hydrolysis of the acetyl derivative, prepared from the iodo-acid (VI, $Hal=I$) with potassium acetate, also failed, owing perhaps to the fact that the intermediate acetyl derivative could not be obtained pure. In the hope of purifying some of the intermediate products, the action of phosphorous di-iodide has been tried on ethyl aleuritate. The process is found to be far more satisfactory as the iodo-ester can be purified by distillation. Acetylation with potassium acetate in acetic acid gives the corresponding acetyl derivative, which on hydrolysis with alcoholic potassium hydroxide gives the desired epi-ambrettolic acid, m.p. $55-55.6^\circ$, along with an impurity, m.p. $81-82^\circ$, having a much higher carbon content which is under investigation.

Attempts are made to condense the iodo-ester with sodiomalonic ester and potassium cyanide for synthesising homocivetic (IV $n=n'=7$) and civetic (IV, $n=6$; $n'=7$) acids. Unusual difficulties are, however, encountered in carrying out these apparently simple operations. The desired product could be obtained only under very specific conditions, the slightest variations leading to completely different products.

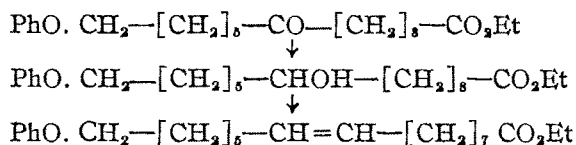
Condensation of the iodo-ester with ethyl sodiomalonate in alcohol results in the isolation of ethyl 16-ethoxy- Δ^9 -hexadecenoate. When the reaction is carried out in benzene medium (*vide* experimental) the triester (VII) is formed which on hydrolysis and decarboxylation followed by esterification and distillation furnishes diethyl ester of homocivetic acid (IV, $n'=n=7$). The crude acid obtained by hydrolysis of the ester with methyl alcoholic potassium hydroxide melts at $81-88^\circ$, the melting point being raised to $102.5-103.5^\circ$ after three crystallisations from ethyl acetate. Ketone to civetone by distillation of the yttrium salt or through the dinitrile by the method of Ziegler will be taken up as soon as a sufficient quantity of the acid has been obtained.

The meagre solubility of crude iodo-ester in alcohol, coupled with its tendency to resinify, leads to poor yields in our attempt to replace the iodine by a cyano group. A number of conditions was tried *e.g.*, potassium cyanide in aqueous alcohol, in acetone or methyl ethyl ketone and silver

cyanide in benzene, but no satisfactory method could be found. The cyano-ester has not been obtained in sufficient quantity to study its hydrolysis to civetic acid.

The synthetical experiments, mentioned above, can not be regarded as complete, before the synthesis of aleuritic acid itself has been accomplished. Some progress towards the synthesis of this acid was made in this laboratory by Mitter and Dutt who synthesised ethyl 16-acetoxy-10-ketopalmitate (*J. Indian Chem. Soc.*, 1939, **16**, 673).

Meanwhile we have achieved a partial synthesis by preparing 16-phenoxy- Δ^9 -hexadecenoate (m.p. 59°) by the action of sodium phenate on the iodo-ester. We expected that this acid could be obtained synthetically by the reduction of $\text{PhO}\cdot\text{CH}_2[\text{CH}_2]_8\text{CO}[\text{CH}_2]_8\text{CO}_2\text{Et}$ followed by dehydration and hydrolysis.



Unfortunately, the keto-ester could not be reduced either catalytically or with sodium and alcohol. Reduction with aluminium isopropylate gives a compound whose analytical data do not correspond with those required by the hydroxy ester.

EXPERIMENTAL.

Preparation of Aleuritic Acid.—Lac (300 g.) was dissolved in 6*N*-potassium hydroxide (1380 g.) and left to stand for 4 days, when the potassium salt of the acid precipitated. It was filtered, washed with 6*N*-potassium hydroxide, and acidified with 10% ice cold sulphuric acid. The light yellow coloured acid was crystallised from water with a little charcoal, m.p. $100\text{--}101^\circ$. The yield was 10%.

ω -Iodo- Δ^9 -hexadecenoic acid was prepared by adding a carbon-disulphide solution of phosphorus di-iodide to an ethereal suspension of aleuritic acid (10 g. in 60 c.c.). There was some effervescence and a sticky red solid was formed. After standing overnight ice was added and it was extracted with ether and washed with sodium thiosulphate. It was obtained as a thick oil, which could not be purified but was directly used for the next process.

Addition of solid phosphorus di-iodide (*cf.* Kuhn and Winterstein, *loc. cit.*) to an ethereal suspension of aleuritic acid gave inferior results.

Epi-ambrettolide was obtained by refluxing the silver salt of above iodo-acid, prepared as usual from the corresponding ammonium salt, in dry xylene for 36 hours in an oil-bath. The xylene solution was washed with $N/2$ -potassium hydroxide and on removal of xylene a small quantity of an oil (b.p. 165° - $175^{\circ}/10$ mm.) was obtained. (Found: C, 76.4; H, 10.5. $C_{18}H_{34}O_2$ requires C, 76.2; H, 11.1 per cent).

The lactone possesses an intense odour of musk. It decolourises bromine in chloroform and permanganate solution. When freshly distilled it has got a light yellow colour but on standing assumes a brown colour.

Acidification of potassium hydroxide washing of the xylene solution gave *epi-ambrettolic acid* in very impure form.

Ethyl aleuritide was prepared from aleuritic acid using sulphuric acid as usual. The ester crystallised from ether, m.p. 50 - 55° . (Found: C, 65.6; H, 10.5. $C_{18}H_{34}O_6$ requires C, 65.1; H, 10.84 per cent).

Ethyl 16-Iodo- Δ^9 -hexadecenoate.—To a suspension of ethyl aleuritide (20 g.) in dry ether (150 c.c.), a solution of phosphorus di-iodide in carbon bisulphide, prepared by gradually adding iodine (34 g.) to a solution of yellow phosphorus (4.2 g.) in the dry solvent (63 c.c.) was added slowly, a few c.c. at a time, with constant shaking. A sticky mass began to separate. It was then left overnight. The contents of the flask were poured on ice-cold water and extracted with ether. The ethereal layer was washed successively with water, sodium bicarbonate and sodium thiosulphate. On treatment with sodium bicarbonate sometimes a heavy oily layer separated at the bottom. The iodo-ester has a great tendency to resinify. The ether-carbon bisulphide mixture was evaporated under pressure below 50° . It distilled at $180^{\circ}/1.5$ mm, yield 3 g. The yield remained the same when theoretical amounts of phosphorus and iodine were used. (Found: I, 30.3. $C_{18}H_{33}O_2I$ requires I, 31.1 per cent).

Ethyl 16-acetoxy- Δ^9 -hexadecenoate was prepared by refluxing the iodo-ester (14 g.), potassium acetate (15 g.) and glacial acetic acid (45 c.c.) for 5 hours. The mixture was poured into water and extracted with ether. The ethereal extract was washed with sodium bicarbonate, dried and distilled at $190^{\circ}/2$ mm., yield 1 g. (Found: C, 71.3; H, 10.2. $C_{20}H_{36}O_4$ requires C, 70.6; H, 10.6 per cent).

16-Hydroxy- Δ^9 -hexadecenoic acid (*epi-ambrettolic acid*) was obtained by the hydrolysis of the above acetoxy ester with methyl alcoholic potassium hydroxide (10%, 3 mols.), m.p. 55 - 55.5° . It has been observed that if the original iodo-ester is slightly impure, a substance is obtained at this stage, which on crystallisation from acetone and ethyl acetate melts

at 81-82°. This substance is under investigation. (Found: C, 71.7; H, 10.3. $C_{18}H_{30}O_3$ requires C, 71.7; H, 11.1 per cent).

Ethyl Δ^9 -Hexadecene-1: 16 dicarboxylate (ethyl homocivetate).—A suspension of molecular sodium (0.56 g.) in benzene (50 c.c.) was cooled in ice and malonic ester (8 g.) was added to it drop by drop. The mixture was allowed to stand overnight and ethyl 16-iodo- Δ^9 -hexadecenoate in benzene (15 c.c.) was added to the sodio-malonate. It was then allowed to stand one day, next heated at 50°-60° for 8 hours, then on the water-bath for 17 hours and finally in an autoclave for 5 hours at 150° in an atmosphere of alcohol. Benzene and alcohol were removed under low pressure.

To the liquid residue a solution of potassium hydroxide (15 g.) in alcohol (95%, 150 c.c.) was added and the mixture heated on the water-bath for 4 hours, when a red colour developed and the potassium salt of the tricarboxylic acid separated. The mixture was diluted with water and acidified with hydrochloric acid. It was next extracted with ether and then decarboxylated by heating for 1 hour up to 180°. The black tarry mass was esterified with alcohol (20 c.c.) and sulphuric acid (2 c.c., *d.* 1.84) by refluxing for 32 hours. The black mass was poured into ice and extracted with ether, the ethereal extract washed with sodium bicarbonate and distilled, b.p. 210°-215°/3 mm., yield 2.7 g. It is a thick oil, decolourising bromine immediately. (Found: C, 72.04; H, 10.85. $C_{22}H_{40}O_4$ requires C, 71.7; H, 10.9 per cent).

In an experiment where the condensation was carried out in an alcoholic solution in the following manner, ethyl 16-ethoxy- Δ^9 -hexadecenoate was obtained.

The above iodo-ester (5 g.) was added to an alcoholic solution of sodio-malonic ester (malonic ester, 1 c.c.; 0.24 g. of sodium and 4.7 c.c. of alcohol) and the mixture was heated in an autoclave for 2 hours at 145° and for 1½ hours at 150°. The alcohol was driven off and the residue extracted with ether, washed with sodium bicarbonate and distilled. A small quantity of a liquid, which decolourised bromine immediately, was obtained, b.p. 156°/1 mm., while the rest decomposed. (Found: C, 73.4; H, 11.1. $C_{20}H_{38}O_3$ requires C, 73.6; H, 11.6 per cent).

Δ^9 -Hexadecene-1: 16-dicarboxylic acid (homocivetetic acid) was obtained by the hydrolysis of ethyl homocivetate (2.5 g.) with methyl alcoholic potassium hydroxide (15 g. in 15 c.c.).

It crystallised from ethyl acetate, m.p. 102.5°-103.5°. (Found: C, 68.6; H, 9.5. $C_{18}H_{32}O_4$ requires C, 69.2; H, 10.2 per cent).

Ethyl 16-Cyano- Δ^9 -hexadecenoate.—The crude iodo-ester (10 g.) was refluxed with a solution of potassium cyanide (1.8 g.) in alcohol (95%,

90 c.c.) for 3 hours. The alcohol was evaporated off and the product was extracted with ether and distilled, b.p. $190^{\circ}/1$ mm., yield 0.15 g. It is waxy and decolourises bromine immediately, (Found: N, 4.6. $C_{18}H_{33}O_2N$ requires N, 4.56 per cent).

Ethyl 16-Phenoxy- Δ^9 -hexadecenoate.—A solution of the iodo-ester (10 g.) in hot alcohol was added to a solution of sodium phenate in alcohol (sodium, 0.56 g.; alcohol, 10 c.c.; phenol, 2.3 g.) and the mixture heated under reflux for 5 hours. On cooling the whole of the mass solidified. The alcohol was evaporated off and the residue was extracted with small quantities of ether. The ether was evaporated off and the residue distilled at $233-37^{\circ}/3$ mm., when a waxy solid, m.p. $41-43^{\circ}$, was obtained. It decolourises bromine immediately. (Found: C, 77.6; H, 9.68. $C_{24}H_{38}O$ requires C, 77.0; H, 10.16 per cent).

16-Phenoxy- Δ^9 -hexadecenoic acid was obtained by the hydrolysis of the above ester at the ordinary temperature with a 20% solution of potassium hydroxide (3 mols.) in methyl alcohol. After allowing to stand for 5 days the solution was acidified. The acid crystallised from ethyl acetate, m.p. 59° .

We are grateful to Dr. H. K. Sen, Director, Indian Lac Research Institute, Ranchi for the gift of shellac necessary for this investigation.

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IRON-IRON OXIDE ELECTRODE FOR ACID-BASE POTENTIOMETRIC TITRATIONS AND FOR H-ION CONCENTRATION DETERMINATION.

BY BEHARAT RAM AGARWAL AND J. B. JHA.

Iron electrode was tried by McAulay and White (*J. Chem. Soc.*, 1930, 194) for the determination of H^+ ion concentration. His results were irregular especially beyond p_H 7 i.e., in the alkaline solutions.

As iron is one of those elements not attacked by alkalis, it was thought desirable to study the same for its use in alkaline as well as acidic solutions. The electrodes studied were really iron-iron oxide electrodes prepared by various methods. Those found more satisfactory are given below :—

(i) Iron oxide was deposited on a mild steel wire by treating it with fuming nitric acid (d r'4) and subsequently boiling with distilled water for an hour and keeping in dilute acetic acid for a day. The electrode prepared in this way attained a steady potential within a few minutes when placed in a $M/5$ -potassium hydrogen phthalate solution. To maintain the potential the wire was left in dilute acetic acid which was found to be quite satisfactory.

TABLE I.

| Time. | R. M. F. | Time. | R. M. F. | Remarks. |
|-------|--------------|---------|----------|---|
| 0 min | -0.635 volts | 20 min. | -0.641 | Electrode attains stability in about two minutes. |
| 2 | -0.640 | 30 | -0.641 | |
| 5 | -0.641 | 60 | -0.641 | |
| 10 | -0.641 | 120 | -0.641 | |

Titration curves with a buffer solution (Britton and Robinson straight line buffer) are shown in Fig. 1.

Acid base titrations can be easily performed by iron-iron oxide electrode as an indicating electrode. R. M. F. changes along with burette readings are shown in Fig. 2. It may be noted that the alkaline solution was added from the burette so that the electrode was always in contact with an acidic solution throughout the titration.

Another electrode that was tried and found satisfactory was prepared by depositing iron electrolytically on a platinum wire from an iron ammonium citrate solution. The deposited layer was oxidised by

putting it in strong nitric acid for five minutes and then washed with distilled water.

The titration curves (i) with Britton and Robinsons' straight line buffer solution and (ii) acid base titrations are shown in Figs. 3 and 4.

FIG. 1.

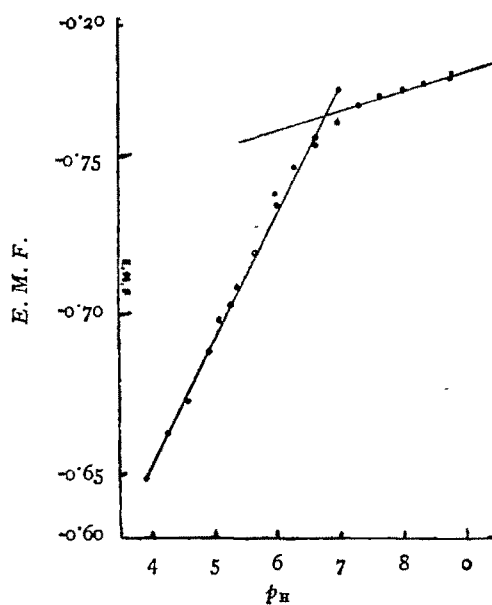


FIG. 2.

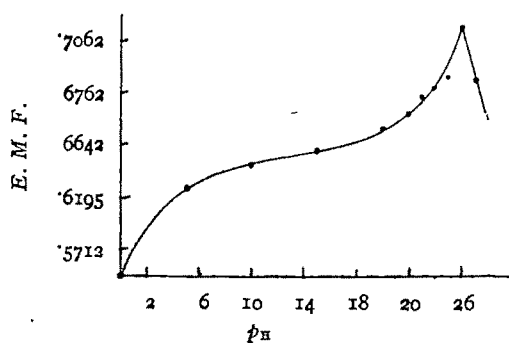


FIG. 3.

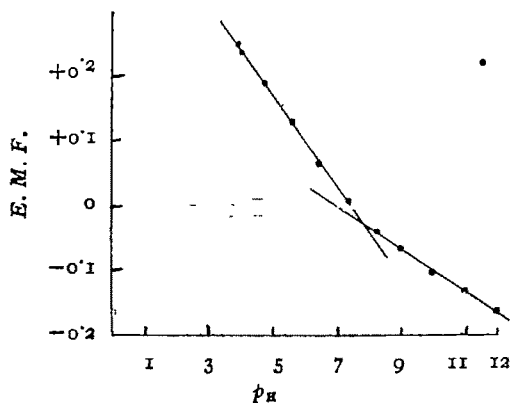
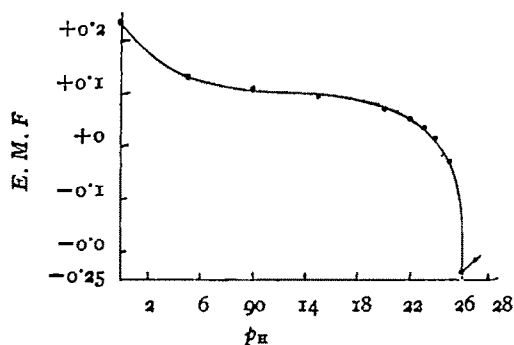


FIG. 4.



It is noteworthy that the titration curves show a break in the neighbourhood of p_H 7 in both the cases.

The relationships observed from a large number of titrations for a mild steel wire oxidised with (i) nitric acid and (ii) electrolytically deposited iron over platinum wire are given below

$$E_1 = -0.4965 - 0.0383 (p_H) \text{ at } 25^\circ. \quad E_1 = +0.527 - 0.0714 (p_H) \text{ at } 25^\circ.$$

$$E_2 = -0.721 - 0.0061 (p_H) \text{ at } 25^\circ. \quad E_2 = +0.237 - 0.0337 (p_H) \text{ at } 25^\circ.$$

The end-point in acid base titrations was shown by a break in the curve and not by an inflexion point.

In alkaline solutions the electrode is not of much use.

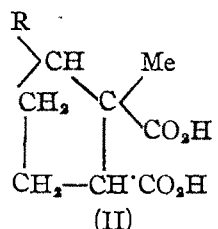
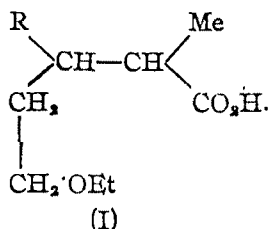
Our thanks are due to Principal H. Krall and Prof. B. L. Vaish for their active interest in the work.

STUDIES IN THE CYCLOPENTANE SERIES. PART II. EXPERIMENTS TOWARDS THE SYNTHESIS OF WIELAND'S C₁₃-ACID IN PROPER STEREOCHEMICAL FORMS.*

BY PHANINDRA CHANDRA DUTTA.

A method for the synthesis of δ -ethoxy- β -(1:5-dimethylhexyl)- α -methylvaleric acid is described.

In continuation of the earlier communication (Dutta, *J. Indian Chem. Soc.*, 1940, 17, 611) the following experiments have been performed to complete the synthesis of Wieland's C₁₃-acid (*Z. physiol. Chem.*, 184, 276; 216, 91) and as a preliminary to it the acid (I) has been synthesised. From this acid by following the method developed in part I an acid of the constitution (II) is expected with the carboxyl groups in the *trans* position, i.e., same as that in the C₁₃-acid.



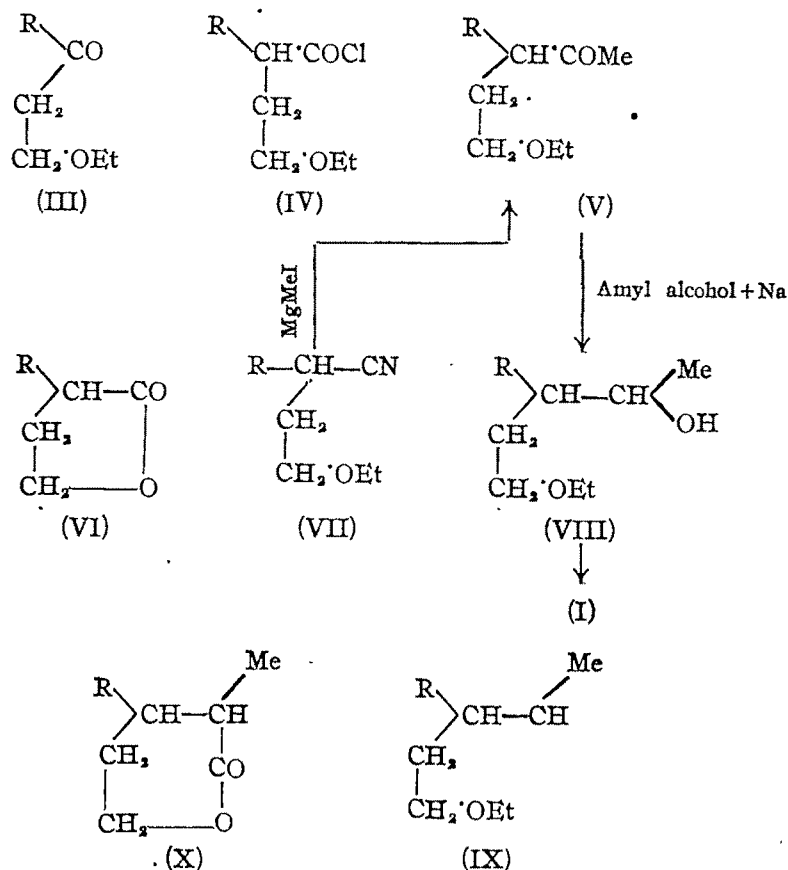
The isopropyl group in (II) can be oxidised by chromic acid according to the well known method of Windaus (*Z. physiol. Chem.*, 117, 146; 126, 277) to give the desired tricarboxylic acid (I). Attempts have been made to prepare the ketone (III), the acid chloride (IV) and the ketone (V) which might be utilised for the synthesis of (I).

The action of methylheptyl magnesium iodide on ethoxyethyl cyanide leads not to (III) but to a hydrocarbon. The formation of Grignard's reagent from ethoxyethyl iodide is also abnormal.

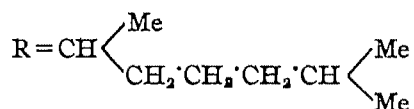
The acid chloride (IV) can not be prepared by the action of thionyl chloride and pyridine on the corresponding acid as the lactone (VI) is formed. To prepare this acid, methylheptyl iodide has been condensed with malonic

* A preliminary note appeared in *Science and Culture*, 1941, 7, 316.

A series of unsuccessful or incomplete attempts are recorded in literature, e.g. Baker (*J. Chem. Soc.*, 1931, 1546; 1933, 811, 815; Bardhan, *Science and Culture*, 1937, 2, 654; Banerjee, *ibid*, 1938, 3, 678).



In all these formulae



ester in presence of sodium ethoxide and ethoxyethyl residue has been introduced through the potassium derivative in xylene solution. This has been hydrolysed to the half ester by heating with an excess of concentrated potassium ethoxide solution (Marshall, *J. Chem. Soc.*, 1931, 2337) and the second ester group has been hydrolysed by the addition of the calculated quantity of water and heating on the water-bath (Claisen, *Ber.*, 1905, 38, 703). The dicarboxylic acid is decarboxylated. The successive replacement of the hydrogen atoms of acetoacetic ester with the heavy substituents methylheptyl and ethoxyethyl in order to produce (V) shows that in whichever order the condensation is attempted, the second condensation does not take place.

The ketone (V) has, however, been obtained by the action of magnesium methyl iodide under the conditions described by Feiser (*J. Amer. Chem. Soc.*, 1936, **58**, 1444, 2482) on the nitrile (VII), which has been prepared thus: methylheptyl iodide has been reacted with cyanoacetic ester in presence of sodium ethoxide with very good yield and the product condensed with ethoxyethyl iodide in presence of potassium in xylene solution. Partial hydrolysis of the disubstituted cyanoacetic ester has been carried out quantitatively by methyl alcoholic potash and on decarboxylation on heating, the substituted nitrile (VII) has been obtained in good yield.

Attempts to prepare the cyanohydrin from this ketone (V) with liquid hydrocyanic acid having failed, it was reduced with amyl alcohol and sodium. The secondary alcohol (VIII), isolated in the usual way, was converted into chloride with thionyl chloride and pyridine. Replacement of the chlorine atom with iodine by boiling with sodium iodide in alcoholic solution leads to the elimination of hydrogen chloride with the formation of the unsaturated compound (IX). The same compound was also obtained while attempting to replace the chlorine atom with cyano group. The desired acid (I) has been obtained through the action of carbon dioxide on the Grignard's complex from the chloro compound. The acid has been purified through its ethyl ester. It is observed that when the concentration of the sulphuric acid in esterification is increased, the ester is contaminated with the lactone (X).

It was expected that this acid (I) should lead to the lactone (X) by the action of pyridine and thionyl chloride and from this lactone, the dibromo ester, necessary for the formation of the cyclopentane ring, will be easily obtainable. This method has, however, led to a neutral product containing halogen and having a higher boiling point than is expected of this lactone. The reaction might have proceeded abnormally (*cf. J. Amer. Chem. Soc.*, 1941, **63**, 2488) and the product has not been further investigated.

EXPERIMENTAL.

Ethyl (1:5-Dimethyl)-hexylacetoacetate.—To a well cooled solution of sodium (16 g.) in alcohol (220 c.c.) was added with shaking a mixture of acetoacetic ester (96 g.) and methylheptyl iodide (158 g.). After allowing it to come to the room temperature and then refluxing on the water-bath for 24 hours, it was decomposed with ice and acid. It was then extracted with ether and washed with sodium bicarbonate, dried and distilled at $122^{\circ}/4$ mm., yield 105 g. It had a characteristic smell. (Found: C, 69.5; H, 10.5. $C_{14}H_{26}O_3$ requires C; 69.4; H, 10.7 per cent).

Ethyl β -Ethoxyethyl-(1:5-dimethyl)-hexylacetoacetate.—Methylheptyl acetoacetic ester (50 g.) was added drop by drop with thorough shaking to an ice-cold suspension of finely powdered potassium (8 g.) in xylene. On standing overnight a clear solution was obtained. To this was added ethoxyethyl iodide (45 g.) with shaking. After heating the mixture on the water-bath for 12 hours, it was refluxed for 24 hours in an oil-bath at 160° . It was then decomposed with ice and thoroughly washed with acid and alkali. After removal of xylene, a small quantity of the high boiling residue was left. This was distilled and two fractions were collected, one boiling at $138-42^{\circ}/3.5$ mm. and the other boiling at $158-60^{\circ}/3$ mm. The former fraction (2.3 g.) on analysis was found to agree with the theoretical values and did not give any ferric chloride colouration. (*Found: C, 68.46; H, 10.8; $C_{18}H_{34}O_4$ requires C, 68.76; H, 10.8 per cent).

Ethyl (1:5-Dimethyl)-hexylmalonate.—It was prepared in the usual way by allowing malonic ester (45 g.) to react with methylheptyl iodide (45 g.) in alcoholic sodium ethoxide solution (4.5 g. sodium and 80 c.c. of alcohol). The reddish solution was decomposed with ice and hydrochloric acid and extracted with ether. The ethereal solution was dried and distilled at $128^{\circ}/4$ mm., yield 39 g. (Found: C, 65.7; H, 9.96. $C_{18}H_{32}O_4$ requires C, 66.1; H, 10.2 per cent).

Ethyl (1:5-Dimethyl)-hexyl- β -ethoxyethyl malonate—To finely powdered potassium (5.1 g.) under xylene was added with shaking methylheptyl malonic ester (37 g.). The formation of the potassium salt was complete on standing overnight. Next it was treated with ethoxyethyl iodide (30 g.) drop by drop. It was heated on the water-bath for 6 hours and for 40 hours again at 150° in the oil-bath. The solution was worked up in the usual way and the residue, left after removal of xylene, was distilled $150-65^{\circ}/5$ mm. This on redistillation passed over at $154-58^{\circ}/5$ mm., yield 22 g. Very careful fractionation was necessary to remove low boiling fractions. (Found: C, 66.36; H, 10.32. $C_{19}H_{36}O_5$ requires C, 66.2; H, 10.4 per cent).

(1:5-Dimethyl)-hexylbutyrolactone (VI).—The above disubstituted malonic ester (26 g.) was treated in the cold with an alcoholic solution of potassium (9.5 g.) in alcohol (65 c.c.). It was allowed to stand overnight and then heated on the water-bath for 24 hours. Water (4.5 c.c.) was then added with shaking and then heating under reflux was continued for another 24 hours. This time crystalline potassium salt separated. The second ester

* Microanalysis by Mr. N. N. Ghosh.

group was hydrolysed by adding water (4.5 c.c.) and heating for another 12 hours. On addition of water, a clear reddish solution was obtained and this was thoroughly extracted with ether to remove any diester, if any, from the solution. The aqueous solution was strongly acidified whereby a heavy oil separated on the surface. It was extracted with ether. The residue, left after the removal of ether, was gradually heated to 220° and kept at that temperature for 1 hour until there were no visible signs of evolution of any gas. It was cooled and a solution of sodium carbonate was added. The alkaline solution was again extracted with ether to remove any mono-ester and the aqueous portion was again acidified with hydrochloric acid, when a heavy oil separated on the surface. It was extracted with ether and on evaporation of ether the residual oil was decolourised with animal charcoal in petroleum ether solution when a mobile oil (15 g.) was obtained having a slight yellowish tinge. This was thoroughly dried and dissolved in benzene and was treated with pyridine (5.3 g.) and thionyl chloride (6.5 c.c.) at low temperature. It was allowed to stand in ice overnight and at the ordinary temperature for 24 hours. Next the clear upper layer was decanted off and distilled when a mobile oil was obtained boiling at $126^{\circ}/5$ mm. having a milky appearance, yield 10 g. It was poured into water and charcoaled when a clear sweet-smelling mobile oil was obtained at $125^{\circ}/4$ mm. The oil was found to be insoluble in sodium carbonate, but soluble in dilute sodium or potassium hydroxide solution from which it could be regenerated by acidification. From concentrated alkaline solution, sodium or potassium salt separated. (Found: C, 72.86, 72.7; H, 10.7, 10.7. $C_{12}H_{22}O_2$ requires C, 72.7; H, 11.1 per cent).

Ethyl (1:5-Dimethyl)-hexylcyanoacetate.—A mixture of cyanoacetic ester (30 g.) and methylheptyl iodide (45 g.) was added to a solution of sodium (4.8 g.) in alcohol (95 c.c.). On refluxing on the water-bath for 12 hours, the red solution was decomposed with ice and the ethereal solution was washed with acid and alkali. On working up in the usual way the cyano ester was obtained, b. p. $125^{\circ}/5$ mm. yield 34.3 g. (Found: N, 6.6. $C_{13}H_{23}O_2N$ requires N, 6.2 per cent).

Ethyl β -Ethoxyethyl-(1:5-dimethyl)-hexylcyanoacetate.—Methylheptyl cyanoacetic ester (34 g.) was added to potassium (5.7 g.) under xylene at 0° drop by drop. On standing overnight a clear solution was obtained. This was cooled in ice and to this ethoxyethyl iodide (35 g.) was added with shaking. The mixture was allowed to stand in ice for 4 hours and at the ordinary temperature for another 4 hours. Next it was heated on the water-bath for 12 hours and in an oil-bath at 160° for 16 hours. The solution was then decomposed with ice and acid. The xylene solution was dried and distilled

at 160-170°/7 mm. On redistillation, it passed over at 165°/7 mm., yield 36 g. (Found : N, 5.1. $C_{17}H_{31}O_3N$ requires N, 4.7 per cent).

(1:5-Dimethyl)hexyl- β -ethoxyethylacetonitrile (VII).—Methyl alcohol (150 c.c.) and the above ester (60 g.) were added to a solution of potassium hydroxide (12 g.) dissolved in the smallest quantity of water. The mixture warmed up and after thorough shaking it was allowed to stand overnight. Next day it was heated on the water-bath for 5 hours. After cooling the mixture was saturated with carbon dioxide. Methyl alcohol was evaporated off and then water added. Traces of neutral matter were removed with ether and the cyano-acid isolated by extracting the acidified solution with ether. The solvent was removed on the water-bath and on heating the residue to 220°, carbon dioxide was evolved. Decarboxylation was complete within an hour. The nitrile, thus obtained, distilled at 127°/5 mm, yield 36 g. (Found : N, 6.6. $C_{14}H_{27}ON$ requires N, 6.2 per cent).

Methyl α -(1:5-Dimethylhexyl)- γ -ethoxypropyl ketone (V).—The above nitrile (22 g.) in dry benzene (100 c.c.) was added all at once to a warm solution of methyl magnesium iodide from magnesium (4.8 g.) and methyl iodide (15 c.c.) containing benzene. After heating on the water-bath for 8 hours it was poured into ice, when a white crystalline solid separated in addition to magnesium hydroxide. After addition of hydrochloric acid, it was refluxed for 4 hours and then subjected to steam distillation. The distillate and the residue in the flask were extracted with benzene and on working up in the usual way, a clear mobile oil having a characteristic smell was obtained boiling at 118°/4 mm. No semicarbazone could be prepared from this ketone and it gave a very slight test for nitrogen. (Found : C, 75.3; H, 12.0. $C_{16}H_{30}O_2$ requires C, 74.4; H, 12.4 per cent).

α -Ethoxy- γ -(1:5-dimethylhexyl)- δ -hydroxypentane (VIII).—The above ketone (18 g.) was dissolved in dry isoamyl alcohol (225 c.c.) and sodium (18 g.) was added. The mixture was heated until the whole of it had gone into solution (about 5 hours). It was diluted with water, amyl alcohol distilled in steam, and the cold solution was extracted with ether and the ethereal extract washed with water and dilute hydrochloric acid. Finally it was dried and distilled at 126°-30°/4 mm, as an oil having a rather unpleasant smell, yield 12 g. (Found : C, 73.7; H, 13.1. $C_{16}H_{32}O_2$ requires C, 74.1; H, 12.9 per cent).

α -Ethoxy- γ -(1:5-dimethylhexyl)- δ -chloropentane.—A benzene solution of the above alcohol (12 g.) was treated with pyridine (4 g.), thionyl chloride (5 c.c.) in the cold. On standing overnight the mixture was refluxed on the water-bath for 3 hours. On working up in the usual way, it passed over at 122-24°/5 mm., yield 12 g. It contained little sulphur which was removed

by refluxing with precipitated copper. (Found: Cl, 12.8. $C_{18}H_{31}OCl$ requires Cl, 13.56 per cent).

α-Ethoxy-γ-(1:5-dimethylhexyl)-Δ^γ-pentene (IX).—(a) The above chloro compound (12 g.) was heated with mercuric cyanide (24 g.) on the water-bath for 1 hour. There was no reaction. Next it was heated in an oil-bath for 3 hours at 160–70°. The substance gradually turned brown. After extraction with benzene, it was finally distilled in *vacuo* when a clear mobile oil boiling at 94°/5 mm. was obtained, yield 6 g. During the latter part of the distillation, volatile mercury compounds began to distill which were removed with hydrogen sulphide in benzene solution. (Found: C, 79.16; H, 13.0. $C_{18}H_{30}O$ requires C, 79.67; H, 13.2 per cent).

(b) The above chloride (22 g.) was refluxed on the water-bath with sodium iodide (26 g.) and alcohol (25 c.c.) and water (1 c.c.) for 24 hours. The mixture gradually became homogeneous. After 24 hours, further alcohol (25 c.c.) was added and the heating continued for another 6 hours. On working up in the usual way, it was found that almost the whole of the product passed over at 95°–103°/6 mm., yield 16 g.

δ-Ethoxy-β-(1:5-dimethylhexyl)-α-methylvaleric Acid (I).—A mixture of the above chloride (15 g.) in ether (15 c.c.) was added to a mixture of magnesium (2.6 g.) in ether (30 c.c.) containing methyl iodide (3 c.c.) at such a rate that the vigour of the reaction was maintained. After the reaction was over, it was refluxed on the water-bath for 3 hours and a current of dry carbon dioxide was passed for 2 hours into the mixture cooled with a freezing mixture. The temperature was kept during this period below –10°. There was a separation of two layers and the mixture was decomposed with ice-cold sulphuric acid. The ethereal extract was separated and washed with a dilute solution of potassium hydroxide. On acidifying the alkaline solution an oil separated having a slight rancid odour. It was extracted with ether and on removal of the solvent, it was dried in vacuum, yield 5.5 g.. The above acid (2.5 g.) was esterified with a mixture of alcohol (25 c.c.) and sulphuric acid (1.5 c.c., *d* 1.84) for 12 hours on the water-bath. On working up in the usual way, the substance boiled at 150–55°/7 mm., yield 2 g. (Found: C, 71.7, 72.1; H, 11.6, 11.7. $C_{18}H_{34}O_2$ requires C, 72.0; H, 12.0 per cent).

The above acid (10 g.) was esterified with alcohol (50 c.c.) and sulphuric acid (7 c.c., *d* 1.84) for 12 hours. On working up in the usual way, a product was isolated (8 g.), b.p. 151–55°/6 mm. This on analysis was found to consist of a mixture of the ethyl ester and the corresponding lactone arising from de-ethoxylation. The latter lactone was not appreciably

soluble in cold alkali. (Found: C, 73.3; H, 11.3. $C_{18}H_{26}O_3$ requires C, 72.0; H, 12.0. $C_{14}H_{20}O_2$ requires C, 74.3; H, 11.4 per cent).

In conclusion, my grateful thanks are due to Prof. P. C. Mitter, Palit Professor and Head of the Department of Chemistry for his valuable suggestions and kind encouragement during the course of these investigations. My thanks are also due to Sir P. C. Ray for his kind interest in this work.

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A NOTE ON THE VOLUMETRIC ESTIMATION OF LEAD.

BY PARES CHANDRA BANERJEE.

Lead iodate, as is well known, is sparingly soluble in water. Alfred and Coolbaugh (*J. Soc. Chem. Ind.*, 1873, 6, 398) worked out a process for the volumetric estimation of lead based upon the precipitation of lead from its solution after slightly acidifying it with nitric acid, with a solution of potassium iodate and then boiling for a few minutes. The precipitate of lead iodate after filtration is dissolved in dilute hydrochloric acid and then titrated in the presence of chloroform with a standard solution of ammonium thiocyanate to the first appearance of violet colour in chloroform. This method, however, suffers from the drawback that small amount of lead iodate tends to pass into solution in time of washing out the excess of potassium iodate.

To avoid the loss of lead iodate during washing the metal has been precipitated by the author as iodate with a moderate excess of a standard solution of potassium iodate excess of which is determined iodometrically by titrating with sodium thiosulphate. The volume of the precipitated lead iodate may seem to cause some error, but this is negligible as the density of lead iodate is 5.4 and its volume never exceeds 0.1-0.2 c.c.

EXPERIMENTAL.

Lead nitrate (28.2921 g.) purified by recrystallisation were dissolved in water and the solution made up to one litre. Its strength was also determined by estimating its lead content as sulphate. A known volume of this solution was taken in a 100 c.c. flask and was diluted with water to about 25 c.c. A measured volume of standard potassium iodate solution (*N*) was added drop by drop from a burette with constant shaking till complete precipitation. Then a few c.c. more of potassium iodate varying from 1 to 10 c.c. were added. The mixture was then made up to 100 c.c., cooled in ice and filtered and in an aliquot part of the filtered solution, excess of iodate was determined by titrating with a standard solution of thiosulphate. The results are given in the following table.

1 C.c. of $N/10$ - KIO_3 soln. = 0.01726 g. of Pb. $Na_2S_2O_3$ soln. = 0.9961 $N/10$.

1 C.c. of $Pb(NO_3)_2$ soln. = 0.01766 g. of Pb.

| Pb $(NO_3)_2$ soln. | KIO_3 added. | $Na_2S_2O_3$ reqd. by excess of KIO_3 . | Amount of Pb | |
|---------------------|----------------|--|--------------|-----------|
| | | | Found | Calc. |
| 10 c.c. | 12 c.c. | 18.0 c.c. | 0.1762 g. | 0.1766 g. |
| 10 | 12 | 17.0 | 0.1765 | " |
| 10 | 20 | 98.0 | 0.1767 | " |
| 10 | 20 | 98.4 | 0.1760 | " |
| 20 | 25 | 45.2 | 0.3538 | 0.3532 |
| 20 | 25 | 45.6 | 0.3531 | " |
| 20 | 22 | 16.6 | 0.3511 | " |
| 20 | 25 | 46.7 | 0.3513 | " |
| 10 | 12 | 18.15 | 0.1758 | 0.1766 |

In the last three determinations lead was precipitated from the hot solution in presence of nitric acid according to Alfred and Coolbaugh's method.

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REVIEW

Recent Advances in Enzymology and Related Subjects. EDITED BY F. F. NORD AND C. H. I. WERKMAN. PUBLISHED BY INTERSCIENCE PUBLISHERS LTD., NEW YORK, 1941. PP. 484. PRICE \$5.50.

During the last two decades the frontiers of our knowledge of enzyme chemistry are being pushed forward so rapidly by armies of investigators all over the world, that it has become difficult to get a unified picture from a reading of the original papers. As early as 1932 the Akademische Verlagsgesellschaft of Leipzig recognised the difficulty and started the publication of the series of *Ergebnisse der Enzyme forschung*. The series now started by the American firm, the Interscience Publishers Ltd., has a similar purpose, that is, to provide a medium of publication in which significant discoveries in enzymology are presented in a more comprehensive and unified fashion than is possible in regular journals, by authors who have been closely identified with this development.

The volume under review appropriately opens with a chapter on protein structure by H. Bull. During recent years some enzymes have been crystallised and characterised as proteins, while others such as the oxidation enzymes have been shown to consist of a protein moiety and an active prosthetic group. The protein is often uniquely fashioned for its specific purpose. Hence the study of protein structure is of special importance in the study of enzyme chemistry. In Part I the author gives a review of the evidence for the peptide linkage being the only important co-valent chemical bond connecting the amino-acid residues. The second part deals with the fibrous proteins and the third part summarises our knowledge concerning the structure of globular proteins. In this section, one finds a summary of the work of Mayer and Mark, Astbury and collaborators, Wyckoff and others on the X-ray diffraction patterns of silk fibroin, keratins and the collagens respectively. We also find an adequate account of the work of Wrinch (1938), who has been noted for her application of mathematics to biochemical problems. Her "cyclol-cage" structure theory of globular proteins has served a worthy purpose, that of stimulating thought. This chapter also includes an excellent summary of the work on the mechanism of denaturation of globular proteins. The chapter on proteinases is written by Max Bergmann and J. S. Fruton who are well known for their pioneer work on the hydrolysis of synthetic peptides and dipeptides.

derived from many kinds of amino-acids. Much valuable information has been gained from such studies regarding (1) the nature of linkages split by proteinases, (2) the specificity of proteinases, (3) kinetics of proteinase activity and (4) the activation of proteinases such as papain, bromelin etc. This chapter gives a review of the above mentioned developments which among many others lead to one fundamental result that of the discarding of the traditional classification of proteolytic enzymes into proteinases and peptidases.

James B. Sumner, the wizard of enzyme purification and crystallisation, has contributed a short account of the chemical nature of crystalline catalase and of the prosthetic groups contained therein. The chapter also deals with the present position regarding our knowledge of the mechanism of catalase action; the views of Haber and Willstätter (1931), Stern (1939) and of Keilin and Hartree (1939) are adequately discussed. A brief mention has also been made of the recent work of Tria on the immuno-chemistry of catalase.

Particular attention may be drawn to the chapter on "Enzymes and Trace substances" in which D. E. Green develops the thought-provoking idea that any substance which occurs in traces in the living cell and which is necessary in traces in diet must be either an essential part of some enzyme or enzyme itself. Vitamins, trace elements like copper, cobalt, manganese, zinc, and magnesium, and hormones are according to Green very possibly the enzymes or prosthetic groups of enzymes. The identification of the anti-neuritic, antirachitic, and B₂ growth vitamins with thiamine, nicotinic acid and flavin, which form the prosthetic groups of oxidation enzymes, has helped to dovetail the field of animal nutrition with that of physiological function. The author also makes a fruitful suggestion concerning the mechanism of the action of many drugs which act at trace concentrations. The belief is expressed that the physiological activity of the drugs is due to their influence on certain specific enzyme systems.

The chapter on "Metabolic generation and utilisation of phosphate bond energy" by Fritz Lipmann gives an account of the recent discovery of phosphate bonds as energy carriers in various metabolic processes. For a long time since the classical work of Harden and Young it was considered that the role of phosphate is essential to facilitate the breakdown of various metabolites by phosphorylation. It is only very recently that a more fundamental and subtle role for phosphate has been recognised. The phosphate bond often serves as a trap for the energy liberated in various metabolic processes and the trapped energy is later on released and utilised for essential purposes of the living cell.

In chapter IV von A. L. Kurssanov has given an able summary of the enzymatic processes in plants and their influence on the growth, draught resistance, nutritional requirements, etc., of plants.

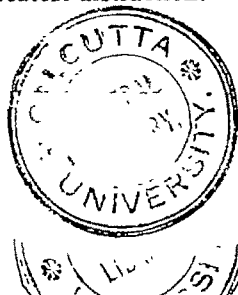
Chapter VII, by J. Franck and H. Gaffron, deals with recent work on photosynthesis, its facts and interpretations. Because of its fundamental importance to life and civilisation the photosynthetic reaction has attracted the attention of numerous able chemists, botanists and physicists for over two centuries, but our knowledge of the mechanism of the photosynthetic reaction and the energy conversion involved therein is still obscure. Yet, the alluring quest is never given up. During the last decade, much work has been done on the quantum yield of the process, the fluorescence phenomena in green plants, induction period in photosynthesis etc. Till very recently it was thought that Warburg and Negelein (1922) have set the final seal on the question of quantum yield. Their result of 4.4 quanta of red light per molecule of carbon dioxide assimilated has been recently challenged by Manning, Stauffer, Duggar and Daniels (1938), Emerson and Lewis (1940) and others who found an average of 12 quanta for the reduction of one molecule of carbon dioxide.

In Chapter VIII, C. B. Van Niel gives a summary of the intensive work carried out during the last decade on photosynthesis by the green and purple sulphur bacteria and discusses the importance of these results for the general problem of photosynthesis in green plants. Van Niel gives a detailed exposition of the rather novel idea, he has developed, that the photosynthetic reactions in green plants and bacteria are only special cases of a more general reaction namely the photochemical carbon dioxide reduction with simultaneous dehydrogenation of some substance H_2A (water in the case of green plants, hydrogen sulphide, sulphur, sulphite, or thiosulphate in the case of sulphur bacteria).

The volume under review contains two other chapters, one by Luise Holzapfel on "Physikalische gesichts punkte zum problem der Virus activitat" and the other on "Die Verdauung bei den niedervertibraten."

The publishers have conferred a great boon on the scientific public by the issue of this volume at a time when we are enveloped in an international crisis which has subjected scientific research to the gravest interruption and original thinking to the greatest distraction.

G. G.

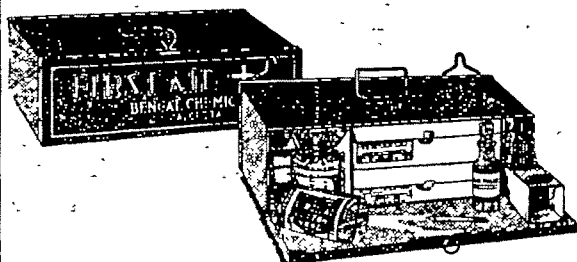


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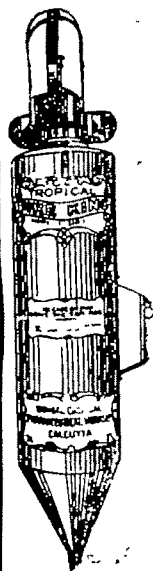
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POSSIBILITIES OF THE PLASTIC INDUSTRY IN INDIA.*

BY PROF. SIR S. S. BHATNAGAR, K.T., O.B.E., D.Sc., F.I.C.,
F.INST.P., F.N.I.

India with her vast natural resources and splendid man-power occupies a rather insignificant position industrially even now. Particularly appalling is the situation with respect to the plastic industry whose rise has justly resulted in the present age being called as the plastic age. Last year a feature of more than ordinary interest was the opening of "Plasti-City" a plastic exhibit, in Washington, sponsored jointly by the Chemical Division of the Department of Commerce in America and the staff of the famous magazine—the Modern Plastics. Every phase of American life from household appliances to national defence preparations was represented in the exhibition. Clothes made from plastics, interior designs and decorations for architectural purposes, plastic applications in the aeronautic and automobiles as well as a whole variety of sporting goods and accessories, raw materials, moulding powder, rods, tubes, sheets and pre-forms were the special features of the show which established beyond doubt the great future of this new and interesting industry.

Just as the dyestuffs industry deals with naturally occurring dyestuffs and synthetic dyes, so can this industry be divided into two parts, namely, naturally occurring resins and synthetic resins. Although the present usage has developed mostly in the form of synthetic resins, as uniformity of product is guaranteed in the synthetic field, there is no doubt that more and more attention will be paid to naturally occurring resins owing to the varying types of uses to which these resins can be put when modified by suitable chemical and physical processes.

Amongst the synthetic resins may be mentioned the following :—

A. CONDENSATION POLYMERS :

1. Resinox, bakelite, durez
2. Beetle or plaskon.
3. Melamine resin.
4. Nylon.
5. Beckosol, glyptal, duraplex.
6. Amberol, beccacite maleic resins.
7. Paraplex.
8. Thiokol.

* Address at the 18th annual general meeting of the Indian Chemical Society, held in Baroda in January, 1942.

B. LINEAR POLYMERS :

1. Styron.
2. Cumar, picco, nevindine.
3. Vistanex.
4. Acryloid.
5. Lucite, crystallite.
6. Gelva, vinylite A.
7. Polyvinyl alcohol.
8. Butvar, butacite, vinylite X YSG.
9. Koroseal.
10. Saran.
11. Neoprene.
12. Buna SS.

C. Co-POLYMERS :

1. Vinylite V
2. Acryloid.
3. Buna S.
4. Perbunan.

1. Resinox, bakelite and durez are prepared by the condensation of phenol and its homologue with formaldehyde, the former being obtained by the interaction of benzene with chlorine and the hydrolysis of chlorobenzene to produce phenol.

2. Beetle or plaskon types of resins are obtained by suitably reacting carbon dioxide gas and ammonia gas to form urea which in turn is condensed with formaldehyde.

3. When nitrogen is passed over calcium carbide under suitable conditions, calcium cyanamide is obtained, and from this compound, cyanamide and melamine are produced. The latter is used as a raw material for several types of melamine resins, such as shellac-melamine resins and those formed by condensation with formaldehyde.

4. The raw material necessary for the production of nylon, which has found the most recent application in the textile industry and which might replace the very popular natural silk fibre, is phenol. Various types of nylons can be obtained depending on the type of acid obtained or employed during the reaction, such as adipic, sebacic acid etc.

5. Naphthalene is the starting material for the production of resins such as glyptal, beckosol and duraplex. When naphthalene is oxidised by air, it forms phthalic anhydride. This anhydride when interacted with a mixture of glycerine and linoleic acid forms the type of resins mentioned above.

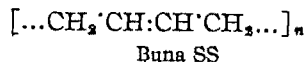
7. Castor oil on dry distillation with sodium hydroxide forms sebacic acid and this acid when suitably reacted with glycerine produces paraplex resins.

9. Thiokol is produced by chlorination of ethylene, and by reacting sodium tetrasulphide with the resultant ethylene dichloride.

11. *iso*Butane on dehydrogenation forms *isobutylene* from which *vistanex* resins are obtained.

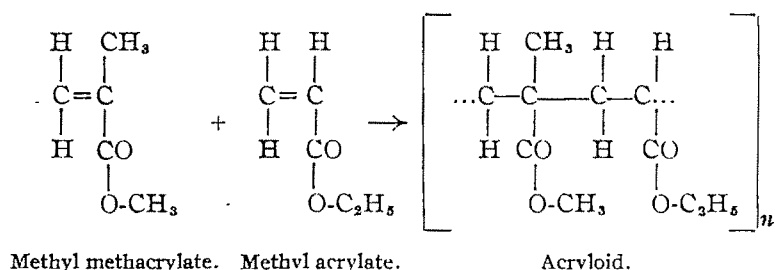
13. Similarly, when acetone is reacted with hydrocyanic acid, acetone cyanohydrin results, which, when interacted¹⁷ with methanol, forms methyl methacrylate, this compound in turn producing lucite or crystallite of commerce.

15. A similar type of linear polyvinyl resins are the polyvinyl chlorides, which are known in commerce as koroseal, saran and neoprene. Koroseal is produced by the combination of ethylene and chlorine gases to form ethylene dichloride which, when reacted with sodium hydroxide, forms vinyl chloride.

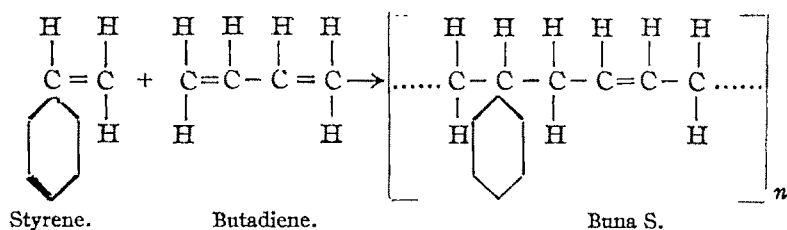
$$\begin{array}{ccccc} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 & \rightarrow & \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2 & \rightarrow & \text{CH}_2 : \text{CH} \cdot \text{CH} : \text{CH}_2 \rightarrow \\ \text{Butane.} & & \text{Butylene.} & & \text{Butadiene.} \end{array}$$


17. VinyliteV forms one of the conjoint polyvinyl resins and is prepared by mixing the required quantities of vinyl chloride and vinyl acetate (see 14) and suitably polymerizing the mixture.

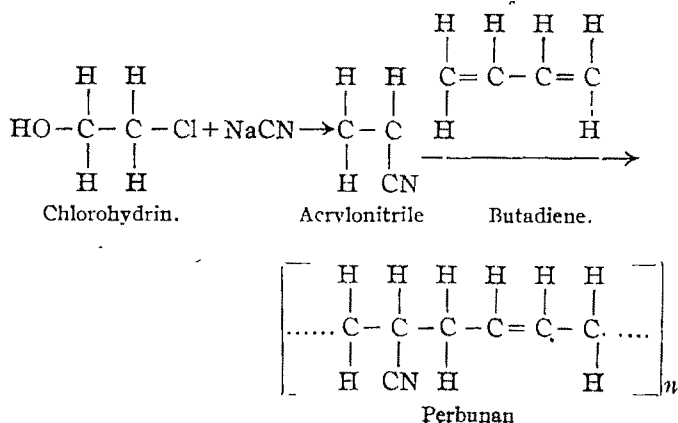
18. Similarly conjoint acryloid polymers are obtained by mixing the required quantities of methyl methacrylate and ethyl acrylate.



19. Another variety of synthetic rubber, Buna S, a copolymeric resin, is prepared by the conjoint polymerization of a mixture of styrene and butadiene as follows:—



20. Perbunan, another variety of copolymeric resins, is prepared by the action of sodium cyanide on chlorohydrin by which acrylonitrile is made, which when polymerized with butadiene produces perbunan resins.



From the above list of the more important resins, one can easily infer what raw materials must be made available in India before the plastic industry can be introduced in this country.

Of these raw materials, perhaps the most important ones are phenol and formaldehyde. Phenols and cresylic acids are produced in reasonable quantities by the Bararee Coke Works and the Shalimar Tar Products. The plant for the manufacture of toluene, set up by the Tatas, ought to result in the further increase of available phenolic bye-products, but these industries must be developed still further to enable India to produce sufficient phenolic substances. Formaldehyde can be produced from methyl alcohol in the dry distillation of wood or it can be synthesised from alcohol. As both methyl and ethyl alcohols are available in this country, there should be no difficulty in producing the necessary formaldehyde. As a result of the impetus given by the Board of Scientific and Industrial Research and Dr. H. K. Sen of the Lac Research Institute, a couple of pilot plants is already manufacturing some formaldehyde. It is quite easy to multiply these plants which can be constructed locally. Amongst other aldehydes, which can be conveniently developed in this country for resin manufacture, may be mentioned furfural. We have obtained good yields of it from rice husk, but there are many other types of cheap cellulosic materials available in India such as water-hyacinth, jute waste etc., and it is quite feasible to manufacture furfural cheaply in this country from any one of these sources.

From the point of view of the plastic industry perhaps the next in order of importance are those resins which depend on urea, calcium carbide and acetylene as the starting materials. For example melamine (see 3) and vinyl resins (see 14 and 17) need calcium carbide and acetylene respectively. The manufacture of calcium carbide industry in this country is an important event. It is gratifying to note that pilot plant work in this connection has been completed and my friend Dr. J. C. Ghosh feels that it is quite feasible for him to make a ton a day of this material in Bangalore itself. Acetylene is an important material not only for the resins but for all metal and engineering industries and we hope that the Government and the public will see to an early establishment of this industry in India. Cheap and abundant supplies of power are the main requisites of this industry. Nylon, the fascinating new resin, can be easily developed as both adipic and sebacic acid can be readily manufactured in this country. The only materials which will have to be developed on the large scale are phenolic products. We are already doing laboratory work on the production of nylon. The cracking process in petroleum industries, now

employed both in Assam and Rawalpindi, can provide starting materials for the development of styrene and synthetic rubber products and will no doubt engage the early attention of oil companies.

Carbon dioxide and ammonia form a set of raw materials for the manufacture of urea-formaldehyde resins such as beetle and plaskon. Carbon dioxide is readily and plentifully available in India. Ammonia, required in the production of urea, is manufactured at present in limited quantities by Messrs. Mysore Chemicals & Fertilizers Ltd. and Messrs. Tata Chemicals Ltd. and it is not unlikely that these firms will be able to meet the demands made by the plastic industry, if required. Ample supplies of glycerine are available in India and the principal firms manufacturing it as a bye-product in the soap industry are Messrs. Tata Oil Mills, Messrs. Lever Bros. and Messrs. Swaika Oil Mills, Lillooha.

It is not for war purposes only that synthetic plastic materials are required in India. It is obvious that a country with such large supplies of vegetable and cracked oil gases, glycerine and cellulosic matter must be deeply interested in the plastic products. The great Jute Industry of Bengal and the growing Textile Industry with its cotton waste and the short-staple cotton and other fibre cultivators urgently feel the need of this industry as without this their bye-products and wastes cannot be suitably developed. The boards, the corrugated sheets and the containers, which can be made from moulding powders, contain fifty or more percentage of this material and fifty per cent of one of these synthetic resins.

In the absence of the synthetic resins Indian workers have addressed themselves to the problem of utilising naturally occurring resin sources for various purposes and it would not be out of place to mention some of the resins which have been successfully developed already. They are as follows:—

1. Lac.
2. Casein.
3. Resins from bagasse and jute waste.
4. Resins from coffee beans
5. Resins from oils.
6. Resins from oil-seed cakes.
7. Resins from horn waste.
8. Resins from *Sarcostemma Brevistigma*.

LAC RESINS

Amongst the naturally occurring resins perhaps lac occupies one of the most important positions. It has been used from times immemorial

but lac as such suffers from several defects which can be cured by chemical and physical treatment. One of the first most important applications which stimulated its export considerably was in the manufacture of gramophone records, which developed during the closing decades of the last century. Since then the export trade has been steadily on the increase. This may be regarded as a direct result of the scientific and industrial research pursued by a number of agencies interested directly in lac production and its consumption.

The first serious programme of research work in this line was laid down by the Indian Lac Research Institute, Namkum which included agricultural, entomological, chemical and physical problems. The U. S. Shellac Importers Association sponsored the New York Shellac Research Bureau which was chiefly concerned with problems of the consumers and those dealing with standardization of the product. Shellac users in Great Britain felt a similar necessity and managed to induce the Indian Lac Research Institute to finance and bring into being the London Shellac Research Bureau, which has produced some of the most important and far-reaching results both in pure and applied fields of lac research. Lastly, the efforts of the laboratories of the Director of Scientific and Industrial Research may be mentioned, which emphasised the development of lac consuming industries in India, a function which had generally taken second place as compared with the activities calculated to assist and encourage the consumers of lac abroad.

In the following paragraphs a brief resume of the results of these researches is presented with a view to indicate how intensive research can help to develop new uses for an age old product like lac and keep its demand alive inspite of the keen competition presented by a flood of synthetic resins now on the market.

One of the early pieces of work done at the Indian Lac Research Institute concerns the use of accelerators in conjunction with lac, which may be looked upon as catalytic agents for promoting the condensation and polymerizing reactions in the resin mass. Thus, small quantities of substance such as urea, thiourea, aluminium chloride, oxalic acid, tetrachlorophthalic acid, phthalic anhydride, sulphanilic acid, dicyanidamine, etc. etc., when added to a lac composition considerably reduce the polymerizing time and improve the product. These researches of Aldis have been made the basis of moulding powders prepared at the New York Shellac Research Bureau and of electric bulb capping cement for use in high speed automatic production. The results of this work have proved useful in a number of other industries as well, where lac need be hardened.

One of very first pieces of work of the London Shellac Research Bureau involved the recognition of the superior properties of hard resin component of lac and the development of new methods for fractionating lac applicable to commercial scale operations. This line of research attracted active attention of other workers in India, America, Germany and other countries, with the result that there now exist at least five distinctly different processes, some of which are being commercially exploited in Germany and Great Britain. The main features of hard lac resin which have made it industrially important include its ease of hardening, higher softening point, low solvent retentivity, capacity to produce hard, flexible and extremely adhesive films, high temperature resistance, freedom from greening of copper when applied as an electrical insulation, low water-sensitivity, etc. The list of its virtues appears to be almost too good to be true, but carefully prepared material has shown all these advantages to exist, and the improvement over original whole lac is definitely marked. As a result of these properties the hard lac resin has found application in numerous industries where quality rather than cost is the chief criterion, for instance as electrical insulation, as tin and aluminium foil lacquers, and others.

Sulphited lac composition developed by the same workers consists of a combination of lac with sulphite through oxonium linkages. It is produced by reaction with alkali bisulphites and sulphites as well as sulphurous acid. The process is unique in as much as it makes possible the deposition of the solid resinous content of a solution in a polymerized insoluble form merely by virtue of evaporation of the solvent. Furthermore, the solution exhibits strong emulsifying power towards oils and fats. Thus the possibilities of its application cover a large field such as water-proof water paints and distempers with or without emulsified drying oils, emulsion-varnishes in water medium for stoving and baking enamels, plastic mouldings, polishes for producing hardened and water-proof films on wood, plaster and metal surfaces, finishes for petrol tanks and containers, sizing materials and polishes with emulsified wax, etc.

Production of oil-lac varnishes, which had been attempted by numerous workers cannot be said to have been successfully accomplished until the London Shellac Research Bureau developed the indirect method of solubilising lac in oil by first dissolving it in fatty acids and then esterifying the solution to produce mixed esters of lac and fatty acids. In this connection one must mention previous attempts of dissolving lac in drying oils at high temperatures through the use of red lead and other agents. Both the processes proved their usefulness, for instance the laboratories of the Director, Scientific and Industrial Research recently opened up two big

fields for its use in anti-gas cloth and in treatment of wood. As a result of these latter developments shellac has found a large market in this country which is bound to expand in the future.

In order to improve film forming properties of spirit varnishes made from lac, it had long been felt that suitable plasticisers must be discovered. First comprehensive study of this problem was made by the New York Shellac Research Bureau, while a more systematic evaluation of various available plasticisers was carried out by the London Shellac Research Bureau and some work was also done at the Indian Lac Research Institute. As a result of these studies certain materials such as sextol, phthalate, *cyclohexanol tartrate*, *p*-toluene sulphonamide and certain others, described by trade names, have been found to be effective. These plasticisers not only impart plastic properties to lac-films, *viz.*, flexibility and resistance against creasing, but also retain or improve such useful properties as are already possessed by ordinary lac films, for instance, water resistance, mechanical strength, adhesiveness, resistance against blushing etc. Consequently the range of application of shellac varnishes is appreciably increased and the quality of products improved, exemplified by such industries as wood polishing, metal finishing, spirit paints, metal foil printing, treatment of textile fabrics, etc.

While dealing with the subject of spirit varnishes, it may be of interest to point out in passing that due to the acidic nature of lac, its spirit solutions have the disadvantage of darkening when stored in metallic containers. To prevent this discolouration, minute quantity of oxalic acid is added which not only prevents the development of dark colour, but actually reduces the colour of varnish by a mere shade. The mechanism of this reaction was studied electrometrically at the London Shellac Research Bureau.

Comparatively recent work of Gidvani and Bhattacharya on the production of esters, ethers and ether-esters of shellac deserves more than a passing mention, for the possibilities of industrial application of these products cover a large industrial field, which include plasticisers, paints and varnishes, linoleum, leather finishes and polishes, rubber like goods, insulating materials, textile impregnants for parachute and anti-gas fabrics, packing and jointing materials, specially elastic paints for rubber surfaces etc.

Another interesting material that has been developed by the London Shellac Research Bureau is the fibrous lac which is obtained in two different forms by the action of formaldehyde on either ammoniacal or on bisulphite solution of lac. The structure of this product indicates the formation of a linear chain molecule which may lead to interesting applications in the

form of extrusion products and spun materials. Used as a basis for varnish manufacture, it yields water resistant and quick drying films.

Combinations of cellulose lacquers with shellac and shellac products have formed a subject of research at different times at all the three lac research organisations at Namkum, New York and London as a result of which considerable data have accumulated which are valuable to the cellulose lacquer industry in assisting it to produce harder, glossier, better weather resistant and more economical lacquers for the trade.

Hot spraying of powdered lac either neat or mixed with addition agents may be regarded as an important industrial development carried out at London. This technique does away with the use of solvent as a vehicle and enables fine films of lac to be deposited on metal, wood, fabric or other surfaces. The troubles arising from the solvent retention nature of lac films, such as water sensitivity etc. are thus automatically eliminated. Possible application of this process includes a whole series of industries where shellac films are applied as protective or decorative coatings, exemplified by laminated products, french polishing, anti-fouling coatings for ship's bottoms, oil storage tanks etc.

So far, one of the chief drawbacks of moulding powders based on shellac had been their inadequacy for use in moulding equipment employed by thermo-setting type of materials such as the phenolics. The latter have a much shorter curing period and the rate of production consequently is high. The newly developed shellac-urea-formaldehyde powders produced by the Indian Lac Research Institute approach very closely the phenolics in this respect and possess other useful characteristics, which make them valuable for industrial exploitation particularly under present day war time conditions.

Other developments of Indian Lac Research Institute include the colourless adhesives made from aleuritic acid, suitable for use in safety glass, shellac-coal tar combinations for the production of moulding powders, plasticine like masses, adhesives and baking enamels, utilisation of destructive distillation products obtained from Kiri for the manufacture of stoving lacquers, shellac-casein moulding powders etc.

Investigations on solvents and solutions of lac at the Indian Lac Research Institute are worthy of note not only from scientific but also industrial point of view. These studies reveal among other things how small quantities of impurities present in solvents improve their solvent power, and how combinations of two non-solvents may constitute a good solvent for lac.

As mentioned earlier, the activities of the laboratories of the Director of Scientific and Industrial Research in relation to lac have been concentrated on the industrial utilization of lac in this country. Towards this goal a number of products have been developed which have made possible the initiation of new industries in India. These include the manufacture of anti-gas cloth, the laminated paper board, the corrugated jute board etc. Other lines of work which are now under way include the resin impregnation of wood, treatment of jute mill bobbins, production of water-proof plywood, all of which have developed far enough to indicate possibilities of commercialization in the very near future.

COFFEE-BEAN PLASTICS.

Before the outbreak of war, India was exporting a large amount of raw coffee to other countries, but on account of the export restriction arising as a result of the outbreak of war the "Coffee Planters Association of India" felt the necessity of finding out some other suitable outlet for their surplus coffee. Perhaps it is well known that coffee beans have been dumped into the sea in Brazil and South America owing to over-production. It was, therefore, suggested to us to undertake an investigation into the possibilities of the utilization of raw coffee for the preparation of moulding powders.

After a year of systematic investigation we have been successful in developing a process for the production of a moulding powder from coffee beans. The outlines of the manufacturing process are as follows:—

The green coffee beans are dried in an oven to facilitate their grinding. Dirt and stones are eliminated by a common flotation process. Broken beans, black beans, sticks or any cellulosic material do not necessarily have to be removed. The powdered coffee beans are made oil-free by refluxing with a suitable solvent. The oil-free powder is subjected to digestion at a fairly high steam pressure with a suitable chemical and in presence of fairly large quantities of water for a certain definite interval of time. The resultant material is washed and ground to a suitable fineness. This powder after mixing with a suitable plasticiser is ready for moulding purposes.

The articles prepared from the above powder are very strong, offer a good resistance to water, take a nice finish and can be drilled, sawed and machined. The flow of coffee bean resins is not quite as good as that of the bakelite type of resins, but investigations show that it can be improved.

This non-beverage use of the surplus and even the poorest quality coffee may provide a new industry.

The bye-products of coffee plastic manufacture are also of interest. Coffee-oil, for instance, is a bye-product which can find many important uses. It is rich in vitamin-D and hence should find use in cosmetics, lotions, medicines and fine quality soaps. It can be used as paint oil or cooking oil. And of course, coffee is a plain source of caffein valuable in medicine and pharmaceutical fields.

OIL-SEED PLASTICS.

Oil seed cakes due to their limited demand as cattle food and organic manure and their bad keeping qualities in tropical climate, but particularly due to the recent export difficulties, drew attention as a subject for the Plastic Industry.

Earlier experiments consisted in the extraction of proteins from the oil cakes by dissolving the former in dilute alkalis and later precipitating with dilute acids. These proteins after hardening by treatment with certain aldehydes, were mixed with suitable fillers, plasticisers, water-proofing agents and finally moulded at definite pressure and temperature.

In another set of experiments the mass left after the protein extraction along with certain basic compounds, was hydrolysed at a fairly high pressure. The product obtained was treated with certain naturally occurring aldehydes and chemicals and later moulded under specific condition of temperature and pressure.

It was observed that mouldings from the second type of experiments were stronger and more water resistant than in the first case. They fairly compare with phenol-formaline products.

RESIN FROM *Sarcostemma Brevistigma*.

The different names ascribed to the *Sarcostemma Brevistigma* are:— Sanskrit and Bombay—Soma ; Hindi and Bengali—Somalata ; Marhatta—Kondopata and in Telgu—Mawa Kiriya. It is also called the Moonplant. It has been described (Dictionary of the Economic Products of India by Watt Vol. VI, pt. II, pp. 477) as a trailing leafless, jointed shrub, not uncommonly met with in dry rocky places in the Deccan Peninsula. It occurs also in Bengal, but more rarely than on the western side of India. Dr. Gibson mentions that "it is often brought from a distance by farmers to extirpate white ants from the sugar fields. A bundle of twigs is put into the trough of the well from which the field is watered along with a bag of salt, hard packed, so that it may dissolve gradually. The water so impregnated destroys the ants without injuring the crop." The plant

contains a large amount of milky sap, which Roxburgh says "is of a mild nature and acid taste, and is often used by Native travellers to allay their thirst. It has been used also in preparing an intoxicating liquor."

It has been possible to prepare a resin from this material by suitable treatment. The softening point of the resin is 60-65°C. The resin, so obtained, is soluble in benzene but not in other common solvents. The resin is capable of yielding a good moulding powder with saw dust and wood powder. Although insoluble in water, it is not so resistant to water action as to compete with other synthetic resins with respect to this quality. By suitable chemical treatments, however, it is possible to improve this property of the resin.

RESINS FROM BAGASSE AND JUTE WASTE.

Cellulosic matter and lignin of which enormous amounts are annually thrown away as a waste product in our sugar mills have drawn the attention of various workers as a source of cheap plastic material. A patent has recently been taken by the Government in which after a thorough and careful investigation of the working conditions, it has been shown that as much as 19% resin can be obtained out of bagasse with little chemical treatment. The broad outlines of the process are given below:

The bagasse from a sugar mill is washed well with water and dried in the open sun. When it is dry, it is powdered either in a grinder or preferably a defibricator to the required mesh. The powdered bagasse is then subjected to steam hydrolysis under pressure in an autoclave. The ratio of water to bagasse, duration of hydrolysis and the temperature and pressure conditions have to be carefully watched and regulated to effect the maximum conversion of the ligno-cellulosic matter into resinous matter. The resin, thus formed within the fibrous cells of bagasse, is extracted by boiling the dry hydrolysed stuff with spirit or alcohol for the pre-determined period. The resin being soluble in spirit is extracted out of the fibrous tissue during the process of refluxing. An alcoholic resinous extract is thus obtained. It has an excess of the solvent and to get rid of it, the alcohol is distilled off. The thick resinous mass is left behind in the retort. Even without alcoholic extraction it is possible to use the fibrous powder as such, as a moulding powder. Should it be necessary to obtain the resin in a powdered form, the last traces of the solvent can be removed over a water-bath. The resin is a dark brown, lustrous mass brittle in nature. It has good binding and water-proofing properties. The melting point varies over a wide range but a fairly average value is

about 148°C. It can be plasticised in the usual manner. Recent investigations show that if the bagasse is hydrolysed in an alkaline or acidic medium, the yield is improved by 2 to 3% with no substantial change in the properties of the resin.

I hope and trust that this survey of some of the important naturally occurring resins and the intensely fascinating synthetic resins will stimulate our Fellows and result in the future expansion of scientific investigations in every direction of this interesting field resulting in the early development of a plastic industry in India worthy of her great natural resources.

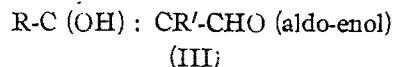
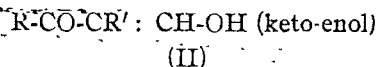
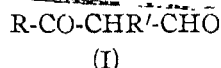
I am much indebted to Dr. L. C. Verman and Mr. S. D. Sunawala for the help in the preparation of this article.

THE VELOCITY OF TRANSFORMATION OF HYDROXY-METHYLENE KETONES INTO BENZENE DERIVATIVES.

BY R. KAUSHAL, (MISS) S. SOVANI AND S. S. DESHAPANDR.

The self condensation of hydroxymethylene acetone and hydroxymethylene acetophenone is a trimolecular reaction, whereas hydroxymethylene methylethylketone does not undergo self condensation and therefore possesses a different structure

Condensation of formic ester with a ketone $R\text{-CO}\cdot\text{CH}_2\text{-R}'$ in presence of sodium or sodium ethylate leads to the formyl derivative (I) which could enolise to (II) or (III).



Claisen and Stylos (*Ber.*, 1888, **21**, 1145) have shown that hydroxymethylene acetone (II, $R=\text{Me}$, $R'=\text{H}$) and hydroxymethylene acetophenone (II, $R=\text{Ph}$, $R'=\text{H}$) undergo automatic condensation into symmetrical triacylbenzenes (*cf.* also Benary, Meyer and Chausius, *Ber.*, 1926, **59**, 108). Hence it was desired necessary to study the reaction mechanism of the transformation with a view to finding out whether such a condensation proceeds with a measurable velocity and whether it has any bearing on the structures of such ketones.

E X P E R I M E N T A L.

Preparation of Hydroxymethylene Ketone.—A mixture of the ketone (1 mol.) and formic ester (1.5 mol.) was added to sodium wire (1.5 atom) in dry ether under ice-cooling. Next day the sodium compound formed was dissolved in water and freed from organic substances by extraction with ether. The aqueous solution of the sodio derivative on decomposition with dilute sulphuric acid liberated the free hydroxymethylene ketone, which was worked up as desired.

These hydroxymethylene ketones are strongly acidic (Claisen, *Ber.*, 1887, **20**, 2191; 1888, **21**, 915). They form chelated copper salt and could be titrated against alkali, while the tri-acyl benzenes are neutral bodies. Therefore the following processes were adopted to study the reaction mechanism.

Copper Titration Process.—The copper compounds of the hydroxymethylene ketones are very soluble in chloroform and sparingly so in water and therefore a direct estimation was not possible.

A definite quantity of the solution of the oxymethylene ketone under examination was pipetted in a separating funnel, to which an excess of copper acetate was added and shaken well. Thereafter the co-ordinated copper compound was extracted thrice with a definite quantity of chloroform (5 c.c.) each time until the extract was colourless. The aqueous copper acetate left unused was titrated with potassium iodide and hypo, starch being used as an indicator (*cf.* also Heiber, *Ber.*, 1921, 64, 902).

This gave us the measure of the hydroxymethylene ketone present at any particular interval. The concentrations being proportional to the volume of the hypo, it was unnecessary to find the actual concentrations.

Alkali Titration Process:—~~The hydroxymethylene ketones are strongly acidic. They could be titrated against an alkali and the titre at any particular moment is a direct measure of the free ketone present at that instant.~~

Therefore a definite quantity of the solution of the oxymethylene ketone was pipetted at definite intervals and titrated against an alkali using phenolphthalein as indicator. Due to sodium salt formation the solution acquired yellow colour at the end-point and hence the solution was diluted enough before titration.

A blank was run under identical conditions with each process in all cases.

TABLE I.

Hydroxymethylene acetone from 5 g. of acetone was dissolved in chloroform, washed, dried and made to 100 c.c. with alcohol. Catalyst = 0.1 c.c. of HCl. 10 C.c. of nearly $N/20$ copper acetate were added to 5 c.c. of the solution at room temperature, and the excess titrated back with 0.034N-hypo.

| Expt. | Hypo | Blank | Time. | $a-x$. | x . | $2a-x$. | $k_2 \times 10^{-4}$. |
|-------|------|-------|--------|---------|-------|----------|------------------------|
| 8.6 | 15.6 | | 0 hrs. | 7.0 | .. | . | .. |
| 10.85 | 15.3 | | 8 1/4 | 4.45 | 2.55 | 11.45 | 7.4 |
| 11.5 | 15.3 | | 25 | 3.8 | 3.2 | 10.8 | 9.7 |
| 12.0 | 15.2 | | 8 1/2 | 3.2 | 3.8 | 10.2 | 9.5 |
| 12.7 | 15.2 | | 137/2 | 2.5 | 4.5 | 9.5 | 10.1 |

The value of the k is fair considering the fact that the experiment is extended for a long period and that the temperature of the room varied between 22° and 27°.

TABLE II.

The ketone obtained from 5 g. acetone as in the Table I, and made to 100 c.c. in chloroform. Catalyst=0.15 c.c. of H_2SO_4 . 25 c.c. of copper acetate were added to 10 c.c. of the solution. Temperature= $49^\circ \pm 1^\circ$. Strength of hypo=0.034N.

| Expt. | Hypo | Blank. | Time. | a-x. | x. | 2a-x. | $k_3 \times 10^{-5}$. |
|-------|------|--------|-------|-------|-------|-------|------------------------|
| 3'55 | 27'2 | 0 min | 23'65 | ... | ... | ... | ... |
| 11'7 | 27'2 | 75 | 15'5 | 8'15 | 39'15 | 1'5 | |
| 12'95 | 27'2 | 110 | 14'25 | 9'4 | 37'9 | 1'4 | |
| 13'6 | 27'2 | 140 | 13'6 | 10'05 | 37'25 | 1'29 | |
| 14'2 | 27'2 | 170 | 13'0 | 10'65 | 36'65 | 1'22 | |
| 15'4 | 27'2 | 215 | 11'8 | 11'85 | 35'45 | 1'25 | |

TABLE III.

To see the effect of concentration the ketone was obtained from 9 g. acetone and made to 100 c.c. in chloroform as in Table II. Catalyst=0.15 c.c. of H_2SO_4 . 10 c.c. solution and 25 c.c. copper acetate. Temperature= $49^\circ \pm 1^\circ$. Strength of hypo=0.034N.

| Expt. | Hypo | Blank | Time. | a-x. | x. | 2a-x. | $k_3 \times 10^{-5}$. |
|-------|------|-------|-------|-------|-------|-------|------------------------|
| 5'5 | 49'0 | 0 min | 43'5 | ... | ... | ... | ... |
| 13'25 | ... | 88 | 35'75 | 7'75 | 79'25 | 1'4 | |
| 14'35 | 49'0 | 130 | 34'65 | 8'85 | 78'15 | 1'17 | |
| 15'95 | ... | 185 | 33'05 | 10'45 | 76'55 | 1'05 | |
| 19'2 | ... | 295 | 29'8 | 13'7 | 73'3 | 1'02 | |
| 19'75 | ... | 370 | 29'25 | 14'25 | 72'75 | 0'91 | |
| 24'0 | 49'0 | 440 | 25'0 | 18'5 | 68'5 | 1'17 | |

TABLE IV.

The ketone obtained from 6 g. acetone and taken up in dry chloroform (100 c.c.). No catalyst. 10 c.c. solution diluted with 50 c.c. water and titrated with 0.0234N-sodium hydroxide. Temperature= $45^\circ \pm 1^\circ$.

| Expt. | NaOH | Blank. | Time. | a-x. | x. | 2a-x. | $k_3 \times 10^{-4}$. |
|-------|------|--------|-------|------|------|-------|------------------------|
| 73'5 | 1'1 | 0 min. | 72'4 | ... | ... | ... | ... |
| 15'0 | ... | 35 | 13'9 | 58'5 | 86'3 | 7'10 | |
| 12'7 | ... | 75 | 11'6 | 60'8 | 84'3 | 3'83 | |
| 11'7 | 1'1 | 110 | 10'6 | 61'8 | 83'0 | 3'96 | |
| 10'2 | ... | 150 | 9'1 | 63'3 | 81'5 | 3'96 | |
| 9'1 | ... | 200 | 8'0 | 64'4 | 80'4 | 3'86 | |
| 8'3 | 1'1 | 275 | 7'2 | 65'2 | 79'6 | 3'50 | |
| 7'1 | 1'1 | 355 | 6'0 | 66'4 | 78'6 | 3'90 | |

TABLE V.

A solution of hydroxymethylene acetone obtained from 6 g. acetone in ether was dried over sodium sulphate, decolourised with animal charcoal, filtered and made up to 150 c.c. with absolute alcohol. Initially no catalyst was added but even after an hour there was no appreciable change which necessitated the addition of catalyst (0.1 c.c. H_2SO_4); and the time recorded from this moment. 10 C.c. solution were diluted with 50 c.c. water. Temperature = 30° . Sodium hydroxide = 0.0234N.

| Expt. | NaOH Blank. | Time. | $a-x$. | x | $2a-x$ | $k_3 \times 10^{-4}$ |
|-------|----------------|--------|---------|------|--------|----------------------|
| 18.5 | 0.8 | 0 min. | 17.7 | ... | .. | |
| 11.4 | 4.0 | 42 | 7.4 | 10.3 | 25.1 | 1.79 |
| 9.7 | ... | 77 | 5.7 | 12.0 | 22.5 | 1.78 |
| 8.8 | 4.0 | 107 | 4.8 | 12.9 | 22.5 | 1.88 |
| 8.0 | ... | 173 | 4.0 | 13.7 | 21.7 | 1.72 |

TABLE VI.

0.371 G. pure hydroxymethylene methyl ethyl ketone (m. p. 72°) was dissolved in 50 c.c. of 90% alcohol. 5 C.c. titrated against 0.0234N-sodium hydroxide at room temperature without any catalyst.

| | | | | | |
|--------------|-----|------|------|------|------|
| Time in days | ... | 1 | 2 | 3 | 4 |
| NaOH titre | ... | 15.8 | 15.8 | 15.8 | 15.8 |

When, however, a catalyst was added, it did not produce any effect even after four days.

TABLE VII.

A solution of hydroxymethylene acetophenone from 5 g. acetophenone in chloroform was dried and made up to 100 c.c. with dry chloroform. 25 C.c. copper acetate were added to 10 c.c. of solution. Catalyst = 0.1 c.c. HCl. Temperature = 22° - 27° . Hypo = 0.034N.

| Expt. | Hypo Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-6}$ |
|-------|----------------|-------|---------|-------|----------|----------------------|
| 19.65 | 42.7 | 0 hr. | 23.05 | ... | ... | ... |
| 21.1 | ... | 17 | 21.6 | 1.45 | 44.65 | 7.7 |
| 21.9 | ... | 24 | 20.8 | 2.25 | 43.85 | 9.0 |
| 23.4 | ... | 43 | 19.3 | 3.75 | 42.45 | 9.3 |
| 24.9 | 42.7 | 69 | 17.8 | 5.25 | 40.85 | 9.4 |

TABLE VIII.

A solution of hydroxymethylene acetophenone from 5 g. acetophenone in ether was dried and ether removed. The liquid so left was made to 100 c.c. with absolute alcohol. Catalyst=0.15 c.c. of HCl. 10 C.c. solution were diluted with 50 c.c. water. Temperature=45°. Sodium hydroxide=0.04N.

| Expt | NaOH Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-5}$. |
|------|----------------|-------|---------|-------|----------|------------------------|
| 18.4 | ... | 0 min | 18.4 | ... | ... | ... |
| 15.9 | 1.8 | 67 | 14.1 | 4.3 | 32.5 | 1.55 |
| 14.6 | ... | 136 | 12.8 | 5.6 | 31.2 | 1.15 |
| 14.0 | 1.8 | 165 | 12.2 | 6.2 | 30.6 | 1.14 |
| 13.4 | ... | 198 | 11.7 | 6.7 | 30.1 | 1.10 |
| 13.0 | 1.8 | 230 | 11.2 | 7.2 | 29.6 | 1.10 |

TABLE IX.

Hydroxymethylene compound from 10 g. acetophenone was dissolved in ether, ether removed and the solution made to 100 c.c. in 90% alcohol. Catalyst=0.15 c.c. of HCl. 5 C.c. solution were diluted with 50 c.c. water. Temperature=48°. Sodium hydroxide=0.04N.

| Expt. | NaOH Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-5}$. |
|-------|----------------|-------|---------|-------|----------|------------------------|
| 36.5 | 0.5 | 0 min | 36.0 | ... | ... | ... |
| 32.4 | 4.3 | 60 | 28.1 | 7.9 | 64.1 | 4.12 |
| 30.0 | ... | 118 | 25.7 | 10.3 | 61.7 | 3.15 |
| 28.4 | 4.3 | 150 | 24.1 | 11.9 | 60.1 | 3.16 |
| 27.3 | ... | 180 | 23.0 | 13.0 | 59.0 | 3.11 |
| 26.4 | 4.3 | 210 | 22.1 | 13.9 | 58.1 | 3.04 |
| 24.7 | ... | 270 | 20.4 | 15.6 | 56.4 | 3.02 |
| 23.7 | 4.3 | 300 | 19.4 | 16.6 | 55.4 | 3.14 |
| 22.2 | 4.3 | 370 | 17.9 | 18.1 | 53.9 | 3.17 |

TABLE X.

Hydroxymethylene compound from 10 g. acetophenone was dissolved in 90% alcohol as in Table IX and divided in two equal parts of 100 c.c. each. Catalyst = 0.15 c.c. of HCl. 5 C.c. solution were diluted with 50 c.c. water. Temperature = 35°. Sodium hydroxide = 0.04N.

| NaOH | | Time. | $a-x$ | x | $2a-x$ | $k_3 \times 10^{-6}$ |
|-------|-------|--------|-------|-----|--------|----------------------|
| Expt. | Blank | | | | | |
| 21.8 | 0.2 | 0 min. | 21.6 | ... | ... | ... |
| 21.4 | 2.0 | 74 | 19.4 | 2.2 | 41.0 | 3.46 |
| 20.8 | 2.0 | 138 | 18.8 | 2.8 | 40.4 | 2.50 |
| 20.1 | ... | 173 | 18.1 | 3.5 | 39.7 | 2.62 |
| 19.7 | ... | 204 | 17.7 | 3.9 | 39.3 | 2.57 |
| 18.7 | 2.0 | 276 | 16.7 | 4.9 | 38.3 | 2.61 |
| 18.5 | 2.0 | 308 | 16.5 | 5.1 | 38.1 | 2.50 |

TABLE XI.

Experiment repeated with the other half from Table X under identical conditions. Temperature = 50°.

| NaOH | | Time. | $a-x$ | x | $2a-x$ | $k_3 \times 10^{-6}$ |
|-------|--------|--------|-------|------|--------|----------------------|
| Expt. | Blank. | | | | | |
| 22.8 | 0.2 | 0 min. | 22.6 | ... | ... | ... |
| 19.0 | 1.8 | 82 | 17.2 | 5.4 | 39.8 | 8.68 |
| 17.1 | ... | 157 | 15.3 | 7.3 | 37.9 | 7.36 |
| 16.7 | 1.8 | 185 | 14.9 | 7.7 | 37.5 | 6.90 |
| 15.4 | ... | 247 | 13.6 | 9.0 | 36.2 | 6.98 |
| 15.1 | 1.8 | 271 | 13.3 | 9.3 | 35.9 | 6.82 |
| 14.7 | ... | 293 | 12.9 | 9.7 | 35.5 | 6.91 |
| 14.3 | 1.8 | 322 | 12.5 | 10.1 | 35.1 | 6.90 |

TABLE XII.

Oxymethylene acetone from 12 g. acetone was dissolved in ether, ether removed and the solution made to 240 c.c. in 90% alcohol and divided into two equal parts of 120 c.c. each. Catalyst=1 c.c. of 0.11 *N*-HCl. Temperature=30°. 5 C.c. solution were diluted with 50 c.c. water and titrated with 0.0484*N*-NaOH.

| NaOH | | | | | | |
|-------|--------|--------|---------|-------|--------|------------------------|
| Expt. | Blank. | Time. | $a-x$. | x . | $2a-x$ | $k_3 \times 10^{-7}$. |
| 27.6 | 0.1 | 0 min. | 27.5 | ... | ... | ... |
| 26.5 | 0.2 | 90 | 26.3 | 1.2 | 53.8 | 6.86 |
| 26.0 | 0.2 | 130 | 25.8 | 1.7 | 53.3 | 6.92 |
| 25.6 | 0.2 | 170 | 25.4 | 2.1 | 52.9 | 6.71 |
| 25.0 | 0.3 | 230 | 24.7 | 2.8 | 52.2 | 6.89 |
| | | | | | | Mean 6.84 |

TABLE XIII.

Expt. repeated with other half of 120 c.c. under identical conditions as in Table XII. Temperature = 20°.

| NaOH | | | | | | |
|-------|--------|--------|---------|-------|----------|------------------------|
| Expt. | Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-4}$. |
| 27'6 | 0'1 | 0 min. | 27'5 | ... | ... | ... |
| 26'9 | 0'2 | 91 | 26'7 | 0'8 | 54'2 | 4'42 |
| 26'6 | 0'2 | 130 | 26'4 | 1'1 | 53'9 | 4'33 |
| 26'2 | 0'2 | 170 | 26'0 | 1'5 | 53'5 | 4'61 |
| 25'9 | 0'3 | 227 | 25'6 | 1'9 | 53'1 | 4'48 |
| | | | | | | Mean 4'46 |

An approximate idea as to the temperature coefficient can be obtained from the ratio of the two velocity constants $k_{30}/k_{20}=6.84/4.46=1.53$.

TABLE XIV.

Oxymethylene acetophenone from 10 g. acetophenone was dissolved in ether, ether removed and the solution made to 200 c.c in 90% alcohol. 100 C.c. were taken for each experiment. Catalyst=1 c.c. of 0.11N-HCl. Temperature=30°. 5 C.c. solution were diluted with 50 c.c. water and titrated with 0.0484N-NaOH.

| NaOH. | | | | | | |
|-------|--------|--------|---------|-------|----------|------------------------|
| Expt. | Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-4}$. |
| 24'1 | 0'1 | 0 min. | 24'0 | ... | ... | ... |
| 23'2 | 0'2 | 50 | 22'8 | 1'2 | 47'8 | 1'92 |
| 22'4 | 0'2 | 80 | 22'2 | 1'8 | 46'2 | 1'83 |
| 21'8 | 0'2 | 110 | 21'6 | 2'4 | 45'6 | 1'85 |
| 21'3 | 0'2 | 144 | 21'1 | 2'9 | 45'1 | 1'78 |
| | | | | | | Mean 1'84 |

TABLE XV.

Expt. repeated with other half (100 c.c.) under identical conditions.
Temperature = 20°.

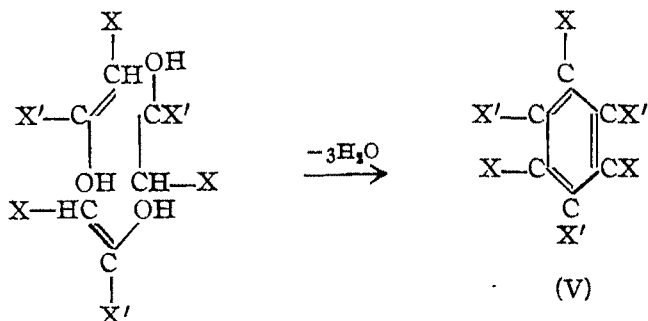
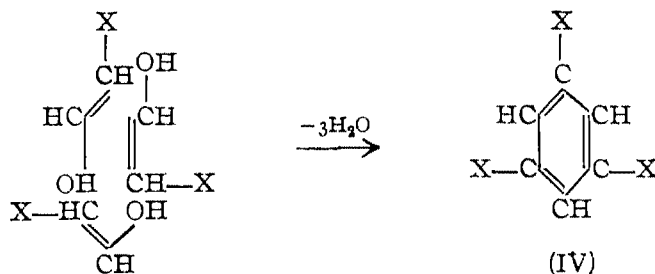
| Expt. | NaOH Blank. | Time. | $a-x$. | x . | $2a-x$. | $k_3 \times 10^{-7}$. |
|-------|----------------|--------|---------|-------|----------|------------------------|
| 24'1 | 0'1 | 0 min. | 24'0 | ... | ... | ... |
| 23'4 | 0'2 | 46 | 23'2 | 0'8 | 47'2 | 1'32 |
| 22'9 | 0'2 | 90 | 22'7 | 1'3 | 46'7 | 1'14 |
| 22'4 | 0'2 | 130 | 22'2 | 1'8 | 46'2 | 1'12 |
| 22'0 | 0'2 | 167 | 21'8 | 2'2 | 45'8 | 1'11 |

Mean 1'17

The ratio of the two velocity constants gives us an approximate idea as to the temperature coefficient of the reaction. $k_{30}/k_{20} = 1'84/1'17 = 1'57$.

DISCUSSION.

It will be clear from the following that the compounds of the type $X\text{-CH:CH-OH}$ and $X\text{-CH:CX'-OH}$ would condense to form tri- or hexa-substituted benzenes (IV) or (V).



Thus a molecule of the hydroxymethylene ketone would undergo automatic condensation into benzene derivative if it contains in its molecule the grouping —CH:CH—OH or —CH:C(OH)— . Conversely a ketone with no such grouping would be stable and would not undergo similar condensation.

Since hydroxymethylene acetone and hydroxymethylene acetophenone are known to undergo self condensation, they must contain in their molecule the grouping —CH:CH—OH or —CH:C(OH)— and hence must possess the structure (II) or (III) (R=Me or Ph ; R'=H). But the final product of condensation is a tri-substituted benzene (IV) (X=CO·Me or CO·Ph) and not hexa-substituted benzene (V) (Claisen, *loc. cit.*), as such structure (II, R'=H) could only be assigned to these compounds.

This is in conformity with the observations of Claisen (*Annalen*, 1894, 281, 309) that of the three forms (II, R=Me , R'=H) is the most stable for acetic aldehyde, as also of Claisen and Stylos (*loc. cit.*) that the compound readily undergoes self-condensation to triacetylbenzene (IV, X=CO·Me), which readily follows from the structure (II).

Similar considerations hold good for hydroxymethylene acetophenone.

Therefore if 'A' represents the molecule of the hydroxymethylene ketone containing the group —CH:CH·OH , condensation to benzene derivative (IV) could take place according to one of the following schemes.

$\text{A} + \text{A} = \text{B}$ (intermediate product still containing the group —CH:CH·OH) + H_2O .



In scheme (i) the two reactions appear to be bimolecular consecutive reactions. It has not been possible to derive an expression connecting t time, k , velocity constant and the concentration of A and B. For, in these cases if A is changing into B and B thereafter into (IV), A can not be measured on account of the fact that B has the same properties as A and the titre at any particular interval will always give the total quantity of A and B present together.

According to the scheme (ii) the reaction is one-sided trimolecular in which the molecules of the same substance are involved. Therefore, if a is the initial concentration of A and after a time t , x of it has changed into (IV), then

$$\begin{aligned} \frac{dx}{dt} &= k_3(a-x)^3 \text{ or} \\ k_3 &= x(2a-x)/2t \cdot a^2(a-x)^3 \end{aligned}$$

Our results show that hydroxymethylene acetone and hydroxymethylene acetophenone undergo self condensation according to the scheme (ii) and the process is a simple trimolecular reaction.

The concentration of the ketone does not affect the velocity constant to any appreciable extent (Tables II and III) but the increase in the temperature increases the velocity constant appreciably (Tables X to XV). This is in agreement with the fact that a very good yield of tribenzoylbenzene (IV, $X = \text{COPh}$) is obtained by heating a solution of hydroxymethylene acetophenone in glacial acetic acid (Claisen, *loc.cit.*). The nature of the solvent has an effect upon the value of the velocity constant, which falls in the following order : chloroform > absolute alcohol > 90% alcohol (Tables IV, V, VIII and IX).

The hydroxymethylene methylethyl ketone was found not to undergo self condensation. It could be distilled and obtained as a white solid. When dissolved in a solvent and titrated it showed no change whatsoever in the titre value (Table VI). Had the substance undergone self condensation, the enol concentration would have decreased and so also the corresponding titre value. Therefore, the substance can not possess the grouping $-\text{CH}:\text{CHOH}$ or $-\text{CH}:\text{C}(\text{OH})-$ and hence must have the structure (II) or (III) ($R = \text{Me} = R'$), reaction taking place at the methylene group marked with an asterisk $-\text{CH}_3-\text{CO}-\overset{*}{\text{CH}}_2-\text{CH}_3$. (cf. also Diels and Ilberg *Ber.*, 1926, **49**, 158). Joshi, Kaushal and Deshapande (*J. Indian Chem. Soc.*, 1941, **18**, 234) from the condensation of the compound with cyanoacetamide have shown that it possesses the structure (II) and not (III).

It is proposed to confirm the observations further by conductivity measurements.

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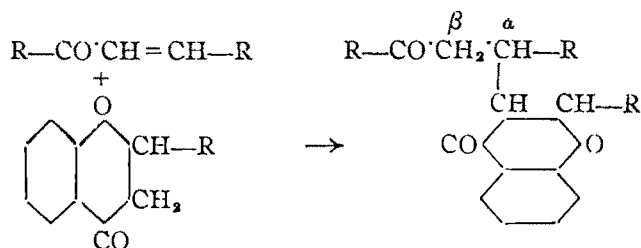
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CONDENSATION OF CHALKONES WITH FLAVANONES.

By B. N. KAPLASH, R. C. SHAH AND T. S. WHEELER.

A number of chalcones and flavanones have been condensed in presence of alkali or pulverised sodium, the latter being particularly effective.

The reactivity of the keto-ethylene group $\text{CH}=\text{CH}\cdot\text{C}=\text{O}$ in chalcones has been the subject of a large number of investigations. Apart from the various reactions they undergo, they give rise to various addition reactions with compounds containing the reactive methylene group (Knoevenagel, *Annalen*, 1894, 281, 25; Hill, *J. Chem. Soc.*, 1935, 1115). Consequently condensation of chalcones with compounds containing the keto-methylene in an open-chain such as acetoacetic ester and desoxybenzoin or in a homocyclic ring like *cyclohexanone* has been extensively studied. No work has, however, been done with compounds having the keto-methylene group in a heterocyclic ring. A study has now been made of the condensation of chalcones with flavanones. The latter contain the $\text{CO}\cdot\text{CH}_2$ group as a part of a ring and it is of interest to see if inclusion in a heterocyclic ring affects the activity of the keto-methylene group. Inclusion in a carbonylic ring as in *cyclohexanone* does not inhibit the addition, and it has now been observed that the flavanones also add on normally as follows —



where R is an aryl radical.

For the present investigation the following condensations were studied.

| Chalkone. | Flavanone. | Condensing reagent |
|---|----------------------------------|--------------------|
| (1) Phenylstyryl ketone | „ | Sodium hydroxide |
| (2) <i>p</i> -Tolylstyryl ketone | „ | „ |
| (3) Phenyl-4'-methoxystyryl ketone | „ | Sodium ethoxide |
| (4) <i>p</i> -Tolyl- <i>p</i> -methoxystyryl ketone | „ | Sodium in ether |
| (5) Phenyl-4'-methylstyryl ketone | „ | „ |
| (6) 4-Methylphenyl-4-methylstyryl ketone. | „ | „ |
| (7) Phenylstyryl ketone | (3':4')-Methylene-dioxyflavanone | „ |

(1) and (2) were successfully condensed by means of aqueous alcoholic sodium hydroxide but in the case of (3) the desired condensation was brought about by employing sodium ethoxide, due to the failure of sodium hydroxide. 4, 5, 6 and 7, however, could not be condensed by means of either of them and therefore resort was made to pulverised sodium in dry ether, which in our opinion is the best condensing agent for such reactions. These compounds were characterised by the formation of their 2:4-dinitrophenylhydrazones.

Flavanone, however, could not be condensed with the following chalkones.

- (1) Phenyl-(3':4') methylenedioxystryl ketone
- (2) *p*-Tolyl-(3':4') methylenedioxystryl ketone
- (3) *o*-Hydroxyphenyl-(3':4') methylenedioxystryl ketone
- (4) *o*-Methoxyphenyl-(3':4') methylenedioxystryl ketone
- (5) 2-Hydroxy-4-methoxy-5-nitrophenylstryl ketone
- (6) 2-Hydroxy-4-methoxy-5-nitrophenyl-4'-methoxystryl ketone
- (7) 2-Hydroxy-4-methoxy-5-nitrophenyl-4'-methylstryl ketone

Thus some chalkones condense readily while others have so far resisted condensation. Although no definite generalisation can be drawn regarding the influence of substituents in the chalkone molecule, it appears that the presence of the (3':4') methylenedioxy group in chalkones retards condensations. The failure of the nitrochalkones to condense may be attributed to the deactivating effect of the nitro group, as had been observed before in similar types of reactions (*cf.* Hutchins, Motwani, Mudphatkal and Wheeler, *J. Chem. Soc.*, 1938, 1882).

EXPERIMENTAL.

The compounds have been numbered for brevity. They were recrystallised from alcohol unless some other solvent is specified. They are all colourless unless otherwise mentioned.

Chalkones.—The following chalkones were prepared from the acetophenone and aldehyde components in presence of alcoholic alkali. (1) Phenylstryl ketone (Kostanecki and Rosbach *Ber.*, 1896, **29**, 1492). (2) *p*-Tolylstryl ketone (Kostanecki and Rosbach, *loc. cit.*). (3) Phenyl-4'-methoxystryl ketone (Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, **39**, 1702). (4) 4-Methylphenyl-4'-methoxystryl ketone (Petrov, *Ber.*, 1930, **63B**, 901). (5) Phenyl-4'-methoxystryl ketone (Hänzlick and Bianchi, *Ber.*, 1899, **82**, 2283). (6) 4-Methylphenyl-4'-methylstryl ketone

(Stobbe and Bremer, *J. pr. Chem.*, 1929, 123, 1). All the chalkones are yellow.

Flavanones.—(7) Flavanone (Ryan and Cruess-Callaghan, *Proc. Roy. Irish Acad.*, 1929, 39, 126). (8) (3':4')-Methylenedioxyflavanone (Ryan and Cruess-Cellaghon. *loc. cit.*). (9) 3-(α -Phenyl- β -benzoylethyl) flavanone. (9) was obtained in the following manner. To an alcoholic solution of 10 g. each of (1) and (7), 2.5 g. of 25% sodium hydroxide solution were added. The mixture was vigorously stirred and allowed to stand in the frigidaire overnight. The solid which settled at the bottom was carefully washed with dilute hydrochloric acid in order to remove away the sodium salt, if any, and filtered, m.p. 149-51°, yield 5 g. (Found. C, 83.2; H, 5.6. $C_{30}H_{24}O_3$ requires C, 83.3; H, 5.6 per cent).

2:4-Dinitrophenylhydrazone of (9) was obtained by heating under reflux an alcoholic solution of (9) and 2:4-dinitrophenylhydrazine. Recrystallised from alcohol-acetone it separated in orange coloured needles m.p. 229-30°. (Found: N, 9.0. $C_{36}H_{28}O_6N_4$ requires N, 9.2 per cent). In the similar manner 3-[α -phenyl- β -(*p*) toluoylethyl] flavanone (10) was isolated from (2) and (7). (Found: C, 83.3; H, 5.8. $C_{31}H_{28}O_3$ requires C, 83.4; H, 5.8 per cent). In exactly the same way as before its 2:4-dinitrophenylhydrazone was obtained. Recrystallised from acetic acid it was obtained as yellowish red needles, m.p. 237-39°. (Found: N, 9.0. $C_{37}H_{30}O_6N_4$ requires N, 8.9 per cent).

3-(α -Anisyl- β -benzoylethyl) flavanone (11) was produced by allowing an alcoholic solution of (3) and (7) to stand overnight in presence of sodium ethoxide, m.p. 92-94°. (Found: C, 79.2; H, 5.4. $C_{31}H_{26}O_4$, $\frac{1}{2}H_2O$ requires C, 79.0; H, 5.7 per cent).

3-(α -Anisyl- β -*p*-toluoylethyl) flavanone (12) was obtained by refluxing for 5 hours ethereal solution of (4) and (7) in presence of a suspension of pulverised sodium. The paste so formed solidified on boiling with alcohol, m.p. 90-92°. (Found: C, 80.6; H, 5.4. $C_{32}H_{28}O_4$ requires C, 80.7; H, 5.9 per cent).

In exactly the same manner as (12), 3-(α -*p*-tolyl- β -benzoylethyl)-flavanone (13) (Found. C, 82.1; H, 6.0. $C_{31}H_{26}O_3$, $\frac{1}{2}H_2O$ requires C, 81.8; H, 6.0 per cent) and 3-(α -*p*-tolyl- β -toluoylethyl) flavanone (14) (Found: C, 80.5; H, 6.2. $C_{32}H_{28}O_3$, H_2O requires C, 80.3, H, 6.3 per cent) were obtained by condensing (5) and (6) with (7) respectively.

2:4-Dinitrophenylhydrazone of (13) of orange colour, m.p. 252-55° (Found: N, 9.2. $C_{37}H_{30}O_6N_4$ requires N, 8.9 per cent) was obtained as

usual. Similarly 2:4-dinitrophenylhydrazone of (14) of orange colour, m. p. $249-51^{\circ}$ was isolated. (Found: N, 8.4. $C_{38}H_{32}O_6N_4$ requires N, 8.8 per cent.) (3':4')-Methylenedioxy-3-(α -phenyl- β -benzoyl ethyl) flavanone (15) was obtained as stated above, by using pulverised sodium as a condensing agent. Recrystallised from acetic acid it melted at $184-85^{\circ}$. (Found: C, 77.7; H, 5.2. $C_{31}H_{24}O_5$ requires C, 78.1; H, 5.0 per cent.) 2:4-Dinitrophenylhydrazone of (15) was obtained as usual by refluxing an alcoholic solution of (15) and 2:4-dinitrophenylhydrazine. Recrystallised from acetic acid it was obtained as orange red needles and melted at $228^{\circ}-30^{\circ}$. (Found: N, 8.2. $C_{37}H_{28}O_8N_4$ requires N, 8.5 per cent.)

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STUDIES IN ENZYMES. PART II. PURIFICATION OF AMYLASE FROM KASERU (*SCIRPUS GROSSUS*, LINN.).

By. J. P. SHUKLA.

Precipitation with ammonium sulphate, dialysis and subsequent precipitation with alcohol gave an active amylase from the herb *Kaseru* (*Scirpus grossus*, Linn.) having a high saccharogenic activity. The purified enzyme isolated has an optimum p_H of 4.8 using acetate buffers.

In a previous paper the author (*J. Indian Chem. Soc.*, 1941, 18, 407) related to the presence of amylase in the tuberous root of the herb *Kaseru* (*Scirpus grossus*, Linn.) and has studied its optimum temperature and p_H . In the present paper an attempt has been made to purify the enzyme and to investigate its nature together with its optimal conditions in the highly purified state.

EXPERIMENTAL.

A fresh lot of *kaseru* was obtained from the market and its skin removed. The white tubers were dried in the sun for 4 days and then ground to powder, sieved through a fine mesh screen and stored for use.

200 G. of starch, thus obtained, were mixed with dry neutral sand and 400 c.c. of 20% alcohol. The mass was kept at 37° for 40 hours and triturated from time to time to extract the enzyme. The filtrate was tested for activity per mg. of the substance. As it is likely that the extract may contain some sugar, the enzyme activity was determined by taking a difference in the weights of Cu_2O precipitated from 5 c.c. of the extract allowed to react without any lapse of time from the Cu_2O precipitated when the extract was allowed to react for exactly one hour at 37° on the same starch solution. The starch solution used was buffered to correspond to the optimum p_H 5.6 as determined in the previous paper.

Diastatic value (Sherman, Kendall and Clerk. *J. Amer. Chem. Soc.*, 1910, 32, 1073) of the extract at 37° for 1 hour is $D^{37}_{1\text{hour}} = 12.2$.

Dialysis of the Extract.—One of the first steps recommended (*J. Amer. Chem. Soc.*, 1926, 48, 2947) for the purification of the enzyme is to dialyse the extract against distilled water in cold using collodion membrane. The specification and use of the membrane has been standardised by various authors (Pierce, *J. Biol. Chem.*, 1927, 75, 795). In the present investigation collodion membrane was prepared using a 6% solution of collodion in ether

and pouring the solution into a conical flask of the required size. The sack obtained was filled with distilled water and immersed for 24 hours in water before use. Several sacks were made under identical conditions and stored for use.

The enzyme extract was dialysed for 24 hours against distilled water at 14°. During dialysis the volume of the liquid in the sack increased from 100 c.c. to 172 c.c. Samples of the dialysate were taken out every hour up to 8 hours and the diastatic activity of the extract measured by Cu_2O precipitation. The dialysate was tested for proteins which are always associated with the amylase to ensure that the enzyme itself has not diffused out completely.

TABLE I.

| Treatment | Molisch test. | Binret test | Cu_2O ppt. | Cu_2O due to extract. | Dry matter | K per g. of solid at 37° for 1 hour. |
|-------------------|---------------|-------------|----------------------------|---------------------------------------|------------|--------------------------------------|
| Blank with starch | — | — | 0.1283 g. | — | — | — |
| Original extract | + | + | 0.3948 | 0.2665 g | 0.2606 g | 31.2 |
| 1 hour dialysis | + | + | 0.2422 | 0.1139 | 0.232 | 163.6 |
| 2 „ „ | + | + | 0.1950 | 0.0667 | 0.206 | 101.6 |
| 3 „ „ | + | + | 0.1664 | 0.0381 | 0.178 | 67.8 |
| 4 „ „ | + | + | 0.1512 | 0.0229 | 0.152 | 44.2 |
| 5 „ „ | + | + | — | — | — | — |
| 6 „ „ | + | + | 0.1455 | 0.0172 | 0.099 | 54.1 |
| 8 „ „ | + | + | — | — | — | 21.6 |
| 24 „ „ | — | — | 0.1293 | 0.0010 | — | — |

It may be seen from the above table that the value of K decreases from 31.2 to 44.2 and then rises to 54.1. On further dialysis it again begins to decrease and comes down to 21.6 after 8 hours' dialysis. The high initial value of K is due to the presence of reducing sugars originally present in the extract. The value of K falls for four hours during the progressive diffusion of the reducing sugars. The increase in the activity of the enzyme, which occurs subsequently, can be traced to the rise in purity. The fall in the value of K after further dialysis shows that during this stage considerable loss of enzyme takes place. A period of 6 hours was, therefore, fixed for dialysis.

Precipitation with Ammonium Sulphate.—At this stage there are two courses that are possible for further purification of the amylase viz., (a) absorption of the amylase on alumina followed by subsequent elution as adopted by Wilstätter (Wilstätter. *et al.*, *Z. physiol. Chem.*, 1923, **121**, 143; 1921 **422**, 72,), (b) precipitation of the amylase by $(\text{NH}_4)_2\text{SO}_4$ of a concentration of 25–35 g. of the salt per 100 c.c. of the extract as recommended by Sherman (Sherman, Caldwell and Doebbeling, *J. Biol. Chem.*, 1934, **104**, 501), followed by dialysis to remove the salt. Since the work of Willstätter in this connection has been criticised by the later workers, the precipitation of the enzyme by $(\text{NH}_4)_2\text{SO}_4$ was adopted.

The dialysate obtained after 8 hours' dialysis was divided into 4 portions of 50 c.c. each and poured over weighed ammonium sulphate in stoppered bottles, well shaken and left for 23 hours in a frigidaire. The supernatant liquid was filtered off by upward microfiltration and the solids washed with alcohol and ether and weighed to get an approximate idea of the yields per 100 c.c. The weighed fractions, obtained at different concentration of the $(\text{NH}_4)_2\text{SO}_4$, were then dissolved in double-distilled water buffered at p_H 5.6 using acetate buffer and made up to 25 c.c. and the activity measured taking 5 c.c. of these solutions.

TABLE II.

| Treatment. | Total moist solids. | Molisch test. | Cu_2O by 5 c.c. extract. | Total solids in 5 c.c. extract. | K per g. solids at 37°. |
|---|---------------------|---------------|--|---------------------------------|-------------------------|
| Extract. | — | + | 0.0104 g. | 0.2606 g. | 12.2 |
| Dialysed 8 hours | — | + | 0.0072 | 0.0994 | 22.2 |
| 20 g. $(\text{NH}_4)_2\text{SO}_4$ per 100 c.c. | 0.5750 g. | Doubtful | 0.0057 | — | — |
| 30 g. „ „ | 0.8298 | + | 0.0162 | 0.0532 | 100.0 |
| 35 g. „ „ | 0.9394 | + | 0.0261 | 0.0405 | 219.2 |
| 40 g. „ „ | 0.9262 | + | 0.0100 | 0.0367 | 89 |

It would be seen from the data that 35 g. of $(\text{NH}_4)_2\text{SO}_4$ per 100 c.c. throw out the maximum quantity of enzyme of the highest activity and this concentration of ammonium sulphate, therefore, appears to be the best that could be utilised. This is also in accordance with the findings of Sherman *et al* (*loc. cit.*).

Precipitation with Alcohol—The enzyme fraction precipitated out by 35 g. of $(\text{NH}_4)_2\text{SO}_4$ was dissolved in a known quantity of double-distilled

water and dialysed till free from SO_4 . Total volume of the solution of enzyme, thus obtained, was kept as low as possible (85 c.c.) and enough absolute alcohol was mixed to obtain the resultant liquid of 50 % alcoholic strength (by vol.). On allowing to stand overnight at 4° in a frigidaire, a precipitate was thrown out which settled at the bottom and was separated by upward filtration. The strength of the solution was then further raised to 60–75% alcoholic strength and the precipitate appearing was separated by upward filtration. It was dissolved in double-distilled water and its activity and optimum p_H determined using acetate buffers (*cf.* Clark, "The Determination of Hydrogen Ions," p. 219).

TABLE III.

Starch concentration = 1.5%. Time of reaction = 1 hour. Temperature = 37° .

| p_H . | K per g. solids | p_H | K per g. solids | p_H . | K per g. solids |
|---------|-----------------|-------|-----------------|---------|-----------------|
| 3.6 | 290.5 | 4.8 | 340.3 | 5.8 | 302.6 |
| 4.2 | 306.8 | 5.1 | 336.8 | 6.2 | 296.3 |
| 4.5 | 320.7 | 5.4 | 318.5 | 6.7 | 290.5 |
| | | | | 7.0 | 286.8 |

The maximum value of the activity of the enzyme after the precipitation from $(\text{NH}_4)_2\text{SO}_4$ was 219.2. As would be seen from the above table the activity increases further to a value of 340.3 after alcoholic precipitation.

The optimum p_H of the amylase in the purified state was found to be 4.8. This value agrees with the findings of Sherman *et al* (*loc. cit.*). The amylase obtained from *Kasera*, was similar to the amylase from malt and had strong saccharogenic activity indicating the presence of β -amylase in larger proportions. Further investigation is in progress to separate the fractions during early stages of ammonium sulphate fractionation to recover the α -amylase possibly having a high amyloclastic activity as against the amylase isolated in a purified state in the present paper.

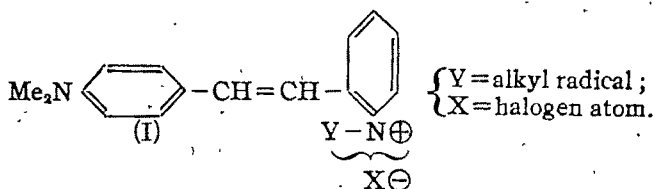
The author acknowledges his thanks to R. C. Srivastava, O.B.E., Director and Dr. H. D. Sen, Biochemist, Imperial Institute of Sugar Technology, Cawnpore for their keen interest and encouragement in the work.

THE CYANINE DYES OF THE PYRIDINE SERIES. PART II.

By M. Q. DOJA AND DHANUSHDHAR PRASAD.

p-Dimethylaminobenzaldehyde has been condensed respectively with α -picoline-methiodide, -ethiodide, -propyl iodide and-butyl iodide; and the chemical, dyeing and photographic properties of the compounds thus produced examined, with a view to investigating the influence of change of structure on the properties of these dyestuffs, specially their sensitising power.

In view of the great importance of 2-*p*-dimethylaminostyrylpyridine alkyl halides (I),



as sensitisers, the influence of the change of anion (*cf.* Kiprianov and Schusser, *Proc. Charcow State Univ.*, 1936, **4**, 49) on the chemical, optical, and photographic properties of the methiodide of (I), was examined by one of us and reported in previous communications (Doja, *J. Indian Chem. Soc.*, 1940, **17**, 347; 1941, **18**, 281). Whereas in those communications X was varied and Y kept unchanged, in the work to be described hereafter, X, the anion, has been kept unchanged (iodide), and Y has been successively replaced by methyl, ethyl, propyl, and butyl, and the properties of the dyes, thus produced, have been examined (*cf.* Mills and Pope, *Photograph. J.*, 1920, **40**, 191; Hamer, Heilbron, Reade and Walls, *J. Chem. Soc.*, 1932, 251). All these dyestuffs were prepared by the condensation of the appropriate quaternary iodide of α -picoline, prepared by slight modifications of the methods of Murril (*J. Amer. Chem. Soc.*, 1899, **21**, 828), with *p*-dimethylaminobenzaldehyde in presence of piperidine (*cf.* Barbier, *Bull. Soc. Chim.*, 1920, **28**, 427; König and Treichel, *J. pr. Chem.*, 1921, **102**, 63; Mills and Smith, *J. Chem. Soc.*, 1922, **121**, 2736; Mills and Raper, *ibid.*, 1925, 2466). They are highly coloured, lustrous, crystalline compounds, showing characteristic reflexes. When examined under a polarising microscope, they exhibit pleochroism, light of one colour being transmitted in one orientation of the polariser, and another colour in an orientation at right angles thereto. These properties of the crystals,

together with their melting points, which show an increase of about 10 degrees as we descend the series, are given in Table I.

TABLE I.

| Name. | M p. | Shape. | Colour by reflected light. | Colour through transmitted light. | Reflex. | Pleochroism. | |
|-------|---------|--------------------|----------------------------|-----------------------------------|-------------------|---|-----------------------------------|
| | | | | | | Colour of light in one position of polariser. | Colour after rotation through 90° |
| (B) | 274° | Needles | Vermilion red | Claret red | Blue | Yellowish red | Nearly opaque |
| (C) | 265° | Rectangular plates | Reddish violet | Orange | Reddish blue | Reddish yellow | Orange-red |
| (D) | 255-56° | Rhombs | Maroon | Orange-red | Greenish blue | Reddish yellow | Dull red |
| (E) | 245° | Laminated plates | Amethyst | Deep orange red | Strong blue-green | Golden red | Opaque nearly |

Being true cyanine dyes, they exhibit the general characteristics of this class of compounds. They are soluble in alcohol and water and insoluble in non-ionising solvents like ether and benzene. The solubility in alcohol and water decreases with increasing molecular weight, the butyl iodide being the least soluble among the four. The solution of these dyestuffs is decolorised by mineral acids and the colour restored by treatment with alkalis.

Aqueous and alcoholic solutions of those compounds are orange-yellow in colour, the yellow component increasing with dilution. The relative intensities of the colour of solutions of these dyes have been determined colorimetrically and the results are shown in Table II. It is interesting to note that there is no regular increase or decrease in colour intensity in the series, the ethiodide forming relatively the most intensely coloured solution.

TABLE II.

| Depth of the solution of | | | | | | |
|--------------------------|-----|------|-------|------|------|------|
| | (B) | (C). | (D). | (E). | | |
| | | 11'5 | 19'2 | 20'3 | | |
| | 15 | 11'4 | 11'46 | 19'3 | 19'3 | 20'3 |
| | | 11'5 | 19'3 | 20'3 | | |
| | | 19'6 | 31'0 | 32'4 | | |
| | 24 | 19'7 | 19'70 | 30'5 | 30'6 | 32'4 |
| | | 19'8 | 30'5 | 32'4 | | |
| | | 1'31 | 0'78 | 0'74 | | |
| Relative intensity | 1 | 1'22 | 1'26 | 0'78 | 0'74 | 0'74 |
| | | | 0'79 | | 0'74 | |

The aqueous solution of these compounds dyes silk, cotton and wool in varying shades of orange-yellow, the reddish tinge of which increases with ascent in the series (Table III). Both neutral and acid solutions have been used, and in each case the same gradation in colour is noticed. The best colour is produced on wool which can be dyed any colour ranging from light lemon-yellow, to deep orange-red by varying the amount of acid added to the dye-bath. These colours, however, are not fast either to soap washing or to sunlight. In the case of washing of silk, it has been observed that the fastness increases as we ascend the series. It has been further noted that wool on exposure to sunlight loses its colour much more slowly than either silk or cotton.

TABLE III.

| Name | Colour produced on Cotton | Silk. | Wool. | Remarks. |
|------|---------------------------|-------------------------------|------------------------|---|
| (B) | Yellow-orange | Bright orange-yellow | Yellow-orange | 1. For cotton and wool both neutral and acid baths were used, the latter always giving a weaker tint than the former. |
| (C) | Deep yellow-orange | Bright yellow-orange | Orange | 2. For silk only weakly acid baths were used |
| (D) | Orange | Bright orange | Orange (reddish tinge) | 3. The increase in reddish tinge with ascent in the series is most prominent in wool. |
| (E) | Deep orange | Bright orange (reddish tinge) | Red-orange | |

TABLE IV.

| Name. | Total range of sensitisation | Range of uniformly intense sensitisation. | Sensitisation. | |
|-------|------------------------------|---|----------------|----------|
| | | | Minimum. | Maximum. |
| (B) | 4250-6100 Å | 4450-5400 Å | 5050 Å | 5300 Å |
| (C) | 4250-6000 | 4400-5400 | 5000 | 5250 |
| (D) | 4250-5750 | 4450-5200 | 5000 | 5200 |
| (E) | 4200-6200 | 4350-5750 | 5050 | 5400 |

In Tables I-IV, B, C, D, E refer respectively to the methiodide, ethiodide, propyl iodide and butyl iodide of the dye.

We acknowledge with pleasure our indebtedness to the Government of Bihar for the grant of a research scholarship to one of us (D. P.). Our thanks are also due to Professor L. M. Chatterjee of the Physics Department for valuable help in taking the sensitisation spectra.

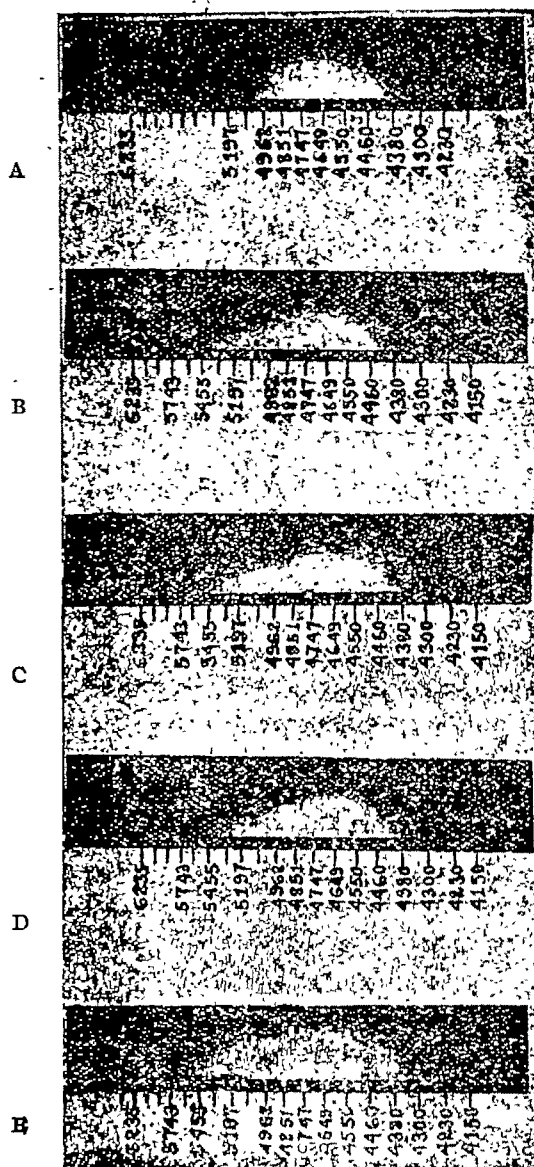


FIG. 1.

EXPERIMENTAL.

Pleochroism.—These were determined by means of a Radial Research Microscope, fitted with a polariser.

The sensitisation spectra of these dyes together with that of an unbathed plate is given in Fig. 1. It will be seen that the butyl iodide shows an uniformly intense band from about λ 4350 to λ 5750. The short gap in the blue-green region, which frequently occurs with sensitisers for the red and yellow region of the spectrum, is not found in this substance. Bearing in mind the comparative ease with which this compound can be obtained in the pure state, we regard it as a better sensitiser for this region than the German product "Pinaflavol". For commercial purposes therefore, we have named 2-*p*-dimethylaminostyrylpyridine-butyl iodide, "Sensitin Z". The methyl and the ethyl compounds give nearly similar spectra, and the propyl compound produces a definitely poorer induced sensitisation. The salient features of the sensitisation spectra of these compounds are shown in Table IV.

Colorimetry.—Duboscq colorimeter was used, the strength of the solution being 1g. of the dye in 250,000 c.c. of rectified spirit.

Dyeing.—Cotton, mordanted with tannic acid and fixed with tatar emetic, "scoured" silk, and carefully cleaned wool were used. The fastness tests were carried out according to the standard prescribed in Colour Index of the Society of Dyers and Colourists.

Sensitisation spectra were taken in the same way as described by Doja (*loc. cit.*), except that the reference scale was set up with the help of an Edser-Butler plate, the wave-lengths of the bands of which were determined by means of a grating spectrometer. The solutions used were 1:25,000 in rectified spirit, and the time of exposure was 3 minutes.

2-p-Dimethylaminostyrylpyridine-ethyl iodide.—*p*-Dimethylaminobenzaldehyde (5 g.), α -picoline ethiodide (2.99 g.), and piperidine (1 c.c.) were dissolved in absolute alcohol (67.5 c.c.) and the solution boiled under reflux for 10 hours. The deep orange solution on cooling deposited a red crystalline substance which was recrystallised from absolute methyl alcohol, yield 5.5 g. (75.3 %). (Found: N, 7.52, 7.58; I, 33.56, 33.58. $C_{17}H_{21}N_2I$ requires N, 7.37; I, 33.42 per cent).

2-p-Dimethylaminostyrylpyridine-propyl iodide.—A solution of α -picoline propyl iodide (4.5 g.), *p*-dimethylaminobenzaldehyde (7.84 g.), and piperidine (1 c.c.) in absolute alcohol (65 c.c.) was boiled under reflux for 6 hours. The orange-red solution was allowed to cool and the solid deposited was recrystallised from methyl alcohol, yield 5.4 g. (80.6%). (Found: N, 7.25, 7.31; I, 32.52, 32.32. $C_{18}H_{23}N_2I$ requires N, 7.11; I, 32.25 per cent).

2-p-Dimethylaminostyrylpyridine-butyl iodide.— α -Picoline butyl iodide (3.3 g.), *p*-dimethylaminobenzaldehyde (1.77 g.), absolute alcohol (35 c.c.) and piperidine (0.5 c.c.) were heated together to a brisk boil in a flask with a condenser. Crystals soon began to separate from the deep orange-red solution, but the heating was continued for 8 hours. The filtered dye was dried in a vacuum desiccator, and recrystallised from absolute methyl alcohol, yield 4.05 g. (84%). (Found: N, 7.01, 7.03; I, 31.07, 30.9. $C_{19}H_{25}N_2I$ requires N, 6.86; I, 31.12 per cent).

MAGNETIC STUDY OF PHOTOTROPIC COMPOUNDS. MAGNETIC SUSCEPTIBILITIES OF *p*-DIMETHYLAMINO- AND *p*-DIETHYLAMINO-PHENYLIMINOCAMPHORS.

BY MAHAN SINGH AND TILAK RAJ DATT.

Changes in the values of magnetic susceptibilities of *p*-dimethylamino- and *p*-diethylamino-phenyliminocamphors with exposure to light have been studied. Attempts have been made to explain the results obtained in the light of the formation of free radicals.

Bhatnagar, Kapur and Hashmi (*J. Indian Chem. Soc.*, 1938, **15**, 512) measured the magnetic susceptibility of a large number of phototropic compounds and did not find any change in the magnetic susceptibility value of these substances on exposure to light. This shows that all of them are perhaps identical in constitution and the difference in colour may be due to their states of aggregation being different.

The view that phototropic change involves a polymerisation or depolymerisation (Padoa, *Atti Acad. Lincei*, 1913, **22**, 1500) also is not supported by these observations. Had there been any polymerisation, it would have been accompanied by a change in the magnetic susceptibility on exposure to light.

The present investigation deals with the magnetic susceptibilities of *p*-dimethylamino- and *p*-diethylamino-phenyliminocamphors (Singh and Singh, *J. Indian Chem. Soc.*, 1935, **12**, 219, 768) both of which are phototropic.

EXPERIMENTAL.

p-Dimethylaminophenyliminocamphor, prepared by the method of Singh and Singh (*loc. cit.*) gives a poor yield with a lot of tarry products which render the separation and purification very difficult. The method was, therefore, modified as follows.

p-Dimethylaminoaniline hydrochloride (25% more than the molecular quantity) was treated with a solution of caustic potash. The free base liberated was extracted with ether and the ethereal solution was repeatedly washed with water. It was then dried over anhydrous calcium chloride and evaporated to a small bulk (5 c. c.). Molecular quantity of camphorquinone and a little anhydrous sodium sulphate were added and the mixture was heated for three hours on the water-bath. After cooling, water was added to precipitate the compound. It was recrystallised from 60% alcohol as a light brown fluffy crystalline mass, m.p. 135.5° after deepening in colour.

p-Diethylaminophenyliminocamphor was prepared by a method exactly similar to the one described above. It was crystallised from dilute alcohol into light orange needles melting at 102.5° to a deep red coloured liquid.

p-Dimethylamino compound is yellow and becomes deep yellow with an orange tinge on exposure to light. *p*-Diethylamino compound is, however, light orange, becoming scarlet on exposure.

p-Dimethylamino Compound.

This compound shows diamagnetism but the value is found to increase gradually till it becomes paramagnetic, if the substance is not protected from light as the following figures indicate.

| Obs. | 1 | 2 | 3 |
|--------------------|--------|--------|--------|
| $\chi \times 10^6$ | -0.883 | -0.322 | +0.980 |

If, however, the substance were kept in the dark, the observed value even after three days was found to be -0.881×10^{-6} i.e. it did not change at all.

It is, however, evident that exposure to light profoundly affected the χ -value of this compound. The influence of exposure to light for different intervals of time was, therefore, studied and the results obtained for two different samples under experimental conditions are represented in Table I.

TABLE I.

| Time of exposure. | Magnetic susceptibility $\times 10^6$ | | | Sample in C_6H_6 soln. |
|-------------------|---------------------------------------|----------------------|-----------------|--------------------------|
| | Sample in bulk No. 1 | Sample in bulk No. 2 | Sample in tube. | |
| 0 min | -0.883 | -0.881 | -0.8808 | -0.8806 |
| 5 | +0.911 | -0.199 | -0.8174 | +1.057 |
| 10 | +1.072 | +1.068 | -0.8032 | +1.082 |
| 15 | +1.077 | +1.088 | -0.7880 | +1.085 |
| 20 | +1.074 | +1.080 | -0.7725 | +1.085 |
| 30 | — | +1.091 | -0.7423 | — |
| 40 | — | — | -0.7430 | — |
| 45 | — | +1.085 | — | — |
| 50 | — | — | -0.7427 | — |
| 60 | — | +1.087 | -0.7432 | — |
| 80 | — | — | -0.7432 | — |

Columns 2 and 3 of Table I represent results for two different samples exposed to light in bulk under identical condition. Column 4 embodies the values when the sample was exposed to sunlight in a tube. In this case the value falls from -0.8808 to -0.7423 after 30 minutes, after which further exposure has no effect. This probably suggests that only the surface layer is affected by light.

With a view to throwing, if possible, further light on the mechanism of this process, magnetic study of the substance in benzene solution was also made (result in column 5, Table I). This substance was dissolved in benzene (A. R. quality) to have 1% solution. The susceptibility value of benzene was previously determined to be -0.7108×10^{-6} . The same values for the solution after exposure to light for different intervals of time were determined, from which the values for the solid solute were deduced according to the formula,

$$\chi_{\text{solid}} = \frac{\chi_{\text{soln}} - \left(1 - \frac{P}{100}\right) \chi_{\text{solvent}}}{P/100}$$

where P represents the weight of the solid compound in 100 g. of the solution. It may be mentioned here that in all the above cases, if the sample be not exposed to light but preserved in the dark, the χ -values obtained do not materially differ from the original value, the values being -0.8774×10^{-6} and -0.8801×10^{-6} for columns 4 and 5 respectively (Table I).

p-Diethylamino Compound.

A similar study was made in the case of *p*-diethyl compound. Table II records the values of magnetic susceptibility when the compound was exposed to light in bulk for different intervals of time and the changes in colour also noted.

TABLE II.

| Time of exposure. | $\chi \times 10^6$. | Colour. |
|-------------------|----------------------|-------------------|
| 0 min. | -0.6988 | Deep yellow |
| 5 | -0.3336 | Brownish red |
| 15 | -0.3087 | " |
| 30 | -0.2406 | Deep brown |
| 45 | -0.2088 | Deep brownish red |
| 60 | -0.2085 | " |
| 75 | -0.2080 | " |

It was noted that the compound, when exposed to light, assumed a scarlet colour, but as soon as it was removed from light, the scarlet colour began to fade. After about twelve hours it regained its original yellow colour.

Hence to determine the χ -value of the compound, when it had the scarlet-red colour, the surface of the compound was exposed to reflected light, while the specimen tube was at the balance and the reading was taken when scarlet-red colour was assumed by the compound.

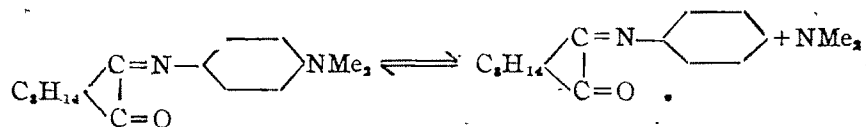
Table III shows the effect of light on the surface of the compound (when the colour was scarlet).

TABLE III.

| Time of exposure. | $\chi \times 10^6$. | Colour. |
|-------------------|----------------------|---------|
| 0 min | -0.6988 | Yellow |
| 5 | +1.738 | Scarlet |
| 10 | +1.7298 | „ |

Singh and Singh (*loc. cit.*) as a result of the study of optical rotations of these two compounds have come to the conclusion that they show geometrical isomerism. Bhatnagar, Mathur and Neogi (*Z. Physik*, 1930, **69**, 373) have, however, shown that although geometrical isomerides show difference in the values of magnetic susceptibility, the difference is not very marked, being, in their case, of the order 0.032×10^7 to 0.052×10^7 only.

The compounds under discussion are diamagnetic to start with and become paramagnetic on exposure to the action of light. This, however, does not support the view that the compound becomes converted into its isomeride and the paramagnetism may be indicative of either polymerisation or the production of free radicals. In the case of styrene, however, Bhatnagar, Kapur and Kaur (*J. Indian Chem. Soc.*, 1940, **17**, 173) have shown that the large change observed in the susceptibility value of styrene on polymerisation cannot be explained only on the constitutional changes involved during the process of polymerisation. They have suggested that under the influence of magnetic field, an isotropic molecule of polystyrene orientates along the lines of force and gives the high susceptibility value observed. A similar view could be advanced in the case of these compounds, but the restoration of the original value on keeping the substances in the dark does not lend support to this. It is, therefore, probable that the substances produce free radicals when exposed to the action of sunlight.



In the free radicals, molecules are supposed to contain an odd number of electrons, which, as is commonly known, results in the paramagnetism of the molecule due to the existence of resultant spin moment. Theoretically the maximum magnetic moment of the substance on exposure to light should approach the value of $2 \times 1.73 = 3.46$ Bohr magneton (since the spin moment of an unbalanced electron in each radical should contribute a value of 1.73 Bohr magnetons). This will hold good only if the conversion is practically complete on exposure to light. It is obvious that the decomposition is only slight and the experimental values of magnetic susceptibilities become constant after a short time (*vide* Table I).

The molecular weight determination of the substance in benzene solution by freezing point method shows no sign of difference before and after exposure to sunlight. This method, as expected, is not of much help to indicate the formation of free radicals as tentatively represented by the equation given above.

The work which presented unusual difficulties as regards the preparation of these compounds is being continued.

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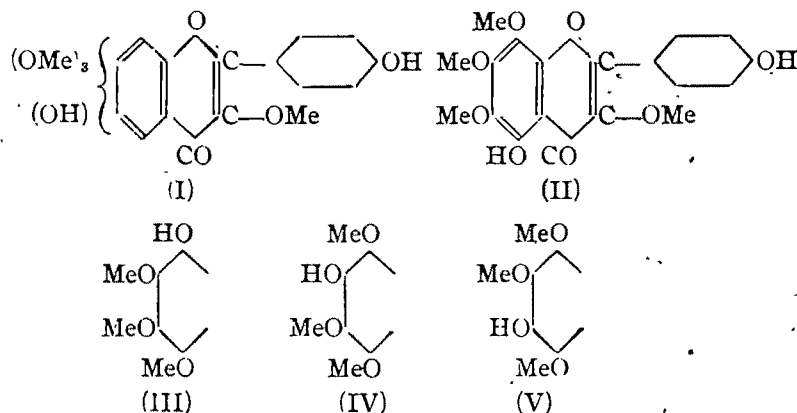


THE CONSTITUTION OF CALYCOPTERIN, THE YELLOW COLOURING MATTER OF THE LEAVES OF *CALYCOPTERIS FLORIBUNDA*

By R. C. SHAH, V. V. VIRKAR AND K. VENKATARAMAN.

The constitution of calycopterin, the yellow colouring matter of the leaves of *Calycopterus floribunda*, is shown to be 5:4'-dihydroxy-3:6:7:8-tetramethoxyflavone, since methylation with diazomethane under stated conditions gives a hydroxypentamethoxyflavone, one hydroxyl thus resisting methylation. Further, the dimethyl ether of calycopterin could be partially demethylated to a hydroxypentamethoxyflavone.

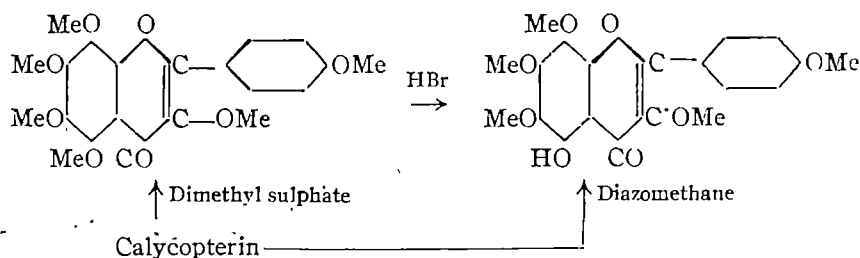
Having partially formulated calycopterin as (I) (Ratnagiriswaran, Sehra and Venkataraman, *Biochem. J.*, 1934, **28**, 1964), four possibilities (II, III, IV, V) remained to be considered. The ease with which calycopterin gave a dimethyl ether, the latter being obtainable also by the action of methyl iodide and potassium hydroxide in methyl alcohol and the preparation



of a dibenzyl ether whose alcoholic solution did not exhibit a colouration with ferric chloride (*cf.* Gulati and Venkataraman, *J. Chem. Soc.*, 1936, 267) appeared to exclude formula (II). On methylation by diazomethane, however, only one hydroxyl group (4') was methylated, and the monomethylcalycopterin, characterised by the formation of an acetyl derivative, exhibited the characteristic properties of a 5-hydroxyflavone, such as intense colouration with alcoholic ferric chloride, insolubility in dilute alkali and the formation of sparingly soluble yellow potassium and sodium salts with alcoholic potassium and sodium hydroxides respectively. As the hydroxyl group is thus shown to be in the 5 position, the three methoxy groups must be in positions 6, 7, 8. Calycopterin was now, therefore, fully formulated

as 5:4'-dihydroxy-3:6:7:8-tetramethoxyflavone (II), the flavone thus falling into line with the suggestion of Bose and Nath (*J. Indian Chem. Soc.*, 1938, 15, 139) that in partially methylated polyhydroxyflavones occurring in nature, the hydroxyl in the 5-position is as a rule not to be found in the methylated condition.

Hydrogen Bromide as a reagent for Preferential Demethylation.—Dimethylcalycopterin was treated with hydrogen bromide in acetic acid at room temperature and the resulting compound was found to be identical with monomethylcalycopterin obtained by methylation of calycopterin with diazomethane, preferential demethylation of the 5-methoxyl group having taken place. This observation is of interest, as hydrogen bromide in acetic acid has not been previously employed for the preferential demethylation of the 5-methoxyl group in flavones, the reagent suggested



earlier being aluminium chloride (Gulati and Venkataraman, *Current Science*, 1933, 2, 50; Gulati and Venkataraman, *loc. cit.*; Mahal and Venkataraman, *ibid.*, 569). An interesting point with regard to this method is that it does not demethylate the 3-methoxyl group as aluminium chloride does (Mahal and Venkataraman, *Current Science*, 1935, 4, 311). In order to confirm that hydrogen bromide in the cold does not attack the methoxyl group in the 3-position, 3-methoxyflavone has been treated with it at room temperature when the ether remains unaffected, but when the reaction mixture is heated on the water-bath, 3-hydroxyflavone is formed. Hydrogen bromide is, therefore, a more facile reagent than aluminium chloride for preferential demethylation.

On the strength of a report from the Pharmacology Research Officer, Medical College, Madras, and the statement of Nadkarni (1927), anthelmintic properties were ascribed to calycopterin in a previous communication (Ratnagiriswaran *et al*, *loc. cit.*). Mahal (*Proc. Indian Acad. Sci.*, 1937, 8A, 186) has more recently studied the anthelmintic action of calycopterin, chrysin, genkwanin (Mahal and Venkataraman, *loc. cit.*), 7-hydroxyflavone and 6-hexyl-7-hydroxyflavone (Dhingra, Uppal and Venkataraman, *Proc. Ind. Acad. Sci.*, 1936, 3A, 206) *in vitro* by directly immersing round worms (*Ascaris lumbricoides*), tape worms (*Tenia serrata*) and leeches (*Hirudo*

medicinalis) in solutions of various concentrations. None of the flavones possesses any anthelmintic or germicidal properties. The Rideal-Walker coefficients are all less than unity.

EXPERIMENTAL.

Two slight modifications in the procedure for the isolation of calycopterin afforded an improved yield (0.23 g. from 100 g. of air-dried leaves). The leaves were not Soxhletted, but refluxed with two lots of acetone; the residue after removal of acetone was vigorously shaken with 150 c.c. of petroleum ether (b.p. 50°-60°) and filtered, the process being repeated thrice.

Calycopterin Dibenzyl Ether.—Benzylation of calycopterin (1 g.) with benzyl chloride (20 g.), potassium carbonate (16 g.) and acetone (150 c.c.) during 32 hours gave the dibenzyl ether, which crystallised from alcohol-acetic acid in pale yellow needles (1.25 g.), m.p. 185°. (Found: C, 71.0; H, 5.6. $C_{33}H_{30}O_8$ requires C, 71.4; H, 5.4 per cent).

Methylation of Calycopterin by Dimethyl Sulphate: Formation of Dimethylcalycopterin (3:4':5:6:7:8-Hexamethoxyflavone).—To a mixture of calycopterin (0.5 g.) and acetone (10 c.c.), dimethyl sulphate (5 g.) and potassium hydroxide solution (15 g. of 30%) were added alternately, keeping the mixture always alkaline. Finally more acetone (5 c.c.) was added and the mixture heated on the water-bath for about $\frac{1}{2}$ hour. The product, which separated on cooling and diluting the mixture with water, crystallised from aqueous acetone in pale yellow needles, m.p. 131°. Ratnagiriswaran and others (*loc. cit.*) recorded the melting point 131° after sintering at 127°.

Methylation of Calycopterin by means of Diazomethane: Formation of Monomethylcalycopterin (5-Hydroxy-3,6:7:8:4'-pentamethoxyflavone).—Calycopterin (0.3 g.) was dissolved in excess of methyl alcohol (30 c.c.); diazomethane in excess (3 mols) dissolved in dry ether was added and the reaction mixture kept at 0° overnight. The yellow solid obtained after allowing ether and alcohol to evaporate was treated with sodium hydroxide (2N). The solid was filtered off at the pump, washed with water and crystallised from absolute alcohol. The substance crystallised in brownish yellow needles, m.p. 124°. With alcoholic ferric chloride solution it gave a fairly deep green colouration. It was practically insoluble in dilute sodium hydroxide, but gave the sparingly soluble yellow potassium and sodium salts with alcoholic potassium and sodium hydroxides respectively. (Found: C, 62.2; H, 5.3. $C_{20}H_{20}O_8$ requires C, 61.9; H, 5.2 per cent).

Demethylation of Dimethylcalycopterin by Hydrogen Bromide in Acetic Acid.—A warm solution of dimethylcalycopterin (0.1 g.) in glacial acetic acid (1.5 c.c.) was treated with 50% hydrogen bromide in acetic acid (1 c.c.) and the reaction mixture was kept overnight. It was then diluted with water and extracted with ether. The ethereal extract was washed first with dilute sodium hydroxide solution and then with water. Ether was allowed to evaporate and the yellowish solid obtained was crystallised from alcohol. It crystallised in brownish yellow needles melting at 124°, not depressed by admixture with the compound obtained by methylation of calycopterin with diazomethane.

5-Acetoxy-3:6:7:8:4'-pentamethoxyflavone.—5-Hydroxy-3:6:7:8:4'-pentamethoxyflavone (0.2 g.) was heated under reflux on a sand-bath with acetic anhydride (1 c.c.) and a few drops of pyridine for 1½ hours. On cooling and diluting with water, the product crystallised from alcohol in colourless needles, m.p. 107°. (Found: C, 61.6; H, 5.0. $C_{22}H_{22}O_8$ requires C, 61.4, H, 5.1 per cent).

Demethylation of 3-Methoxyflavone.—(i) A mixture of 3-methoxyflavone (0.5 g.), glacial acetic acid (4 c.c.) and hydrogen bromide in acetic acid (5 c.c.) was kept for 48 hours at room temperature. It was then diluted with water and the separated product was crystallised from alcohol, m.p. 114°, not depressed by admixture with 3-methoxyflavone.

(ii) A mixture of 3-methoxyflavone (0.5 g.), glacial acetic acid (4 c.c.) and hydrogen bromide in acetic acid (5 c.c.) was heated on the water-bath for 1 hour. It was then diluted with water and the separated product was crystallised from alcohol, m.p. 168-69°; no depression was observed in the mixed melting point of this compound with 3-hydroxyflavone.

(iii) 3-Methoxyflavone (0.5 g.) was thoroughly mixed with excess of anhydrous aluminium chloride (1 g.), and the mixture was heated at 100° for 2 hours. The reaction mixture was then treated with dilute hydrochloric acid, and the dark coloured product was extracted with ether. The ethereal layer was shaken with dilute sodium hydroxide solution, and the alkaline layer acidified with dilute hydrochloric acid. The precipitate when crystallised from alcohol, had m.p. 169° and was identified as 3-hydroxyflavone.

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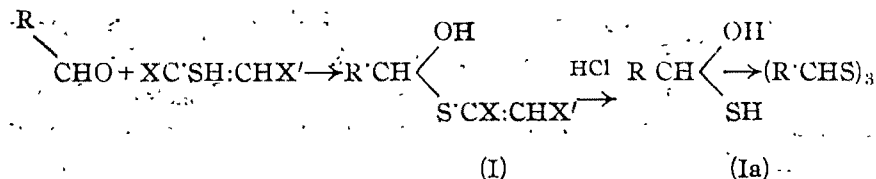
THIOKETONIC ESTERS. PART X.

BY K. CHANDRA, N. K. CHAKRABARTY AND S. K. MITRA.

Cyclic β thioketonic esters have been synthesised and investigated. The mechanism of the reaction of an unsymmetrical triad system with the aldehydes has been established. They have been utilised in the synthesis of hydrothionaphthenes.

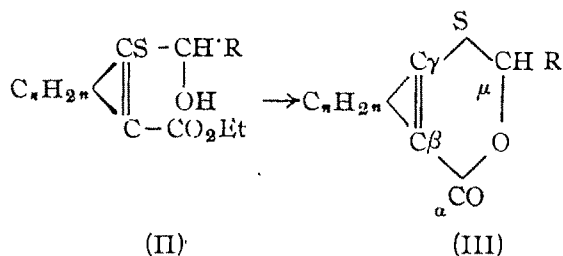
The prototropic system present in chain β -thioketonic esters is in principle very much like that present in their oxygen analogues, excepting that the resonance isomer, which is predominating in the former, is otherwise in the case of the latter as a result of which there is a profound tendency of the former to give rise to S-ethers, and the latter C-ethers during substitution at the reactive centres (Mitra, *J. Indian Chem. Soc.*, 1933, 10, 75 *et seq.*).

Again, there is also a great tendency of "C-C-S" system to release anions in presence of electrophilic reagents and naturally so due to pronounced "T" effect, as the peripheral electrons of sulphur are much further away from the nuclear effect than those of oxygen. This dual nature of a prototropic system could not be observed in system hitherto studied as the members concerned were always simplest members of the groups of periodic table. This great tendency in the case of thioketonic esters to liberate anions (SH^-) always gave difficulty in isolating the intermediate compound (I) which invariably decomposed in the presence of a condensing agent giving rise to thioaldehydes (Mitra, *J. Indian Chem. Soc.*, 1938, 16, 129).



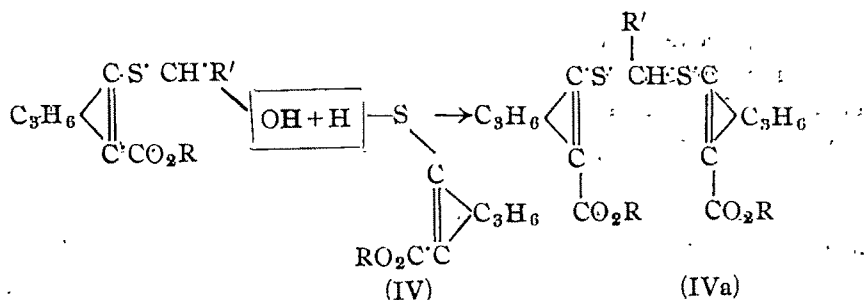
[R and X = alkyl or aryl; X' = CO_2Et].

Due to reasons unknown at present, cyclic thioketonic esters which have been synthesised by the orthodox method (Mitra, *J. Indian Chem. Soc.*, 1933, 10, 71) have been found less susceptible to reagents that help releasing anions from such systems. The alkylated products do not liberate mercaptans even on boiling with acids. They react with aldehydes in the thiol-phase as anticipated giving rise to hydroxy sulphide (II), which soon after



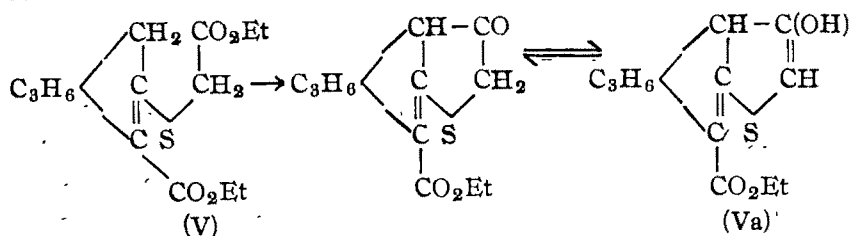
the liberation, lactonises to (III). These lactones are very stable compounds and unlike chain-thioketonic esters cannot furnish the thioaldehydes (Ia). These are new heterocyclic compounds and have been named "metathioxines."

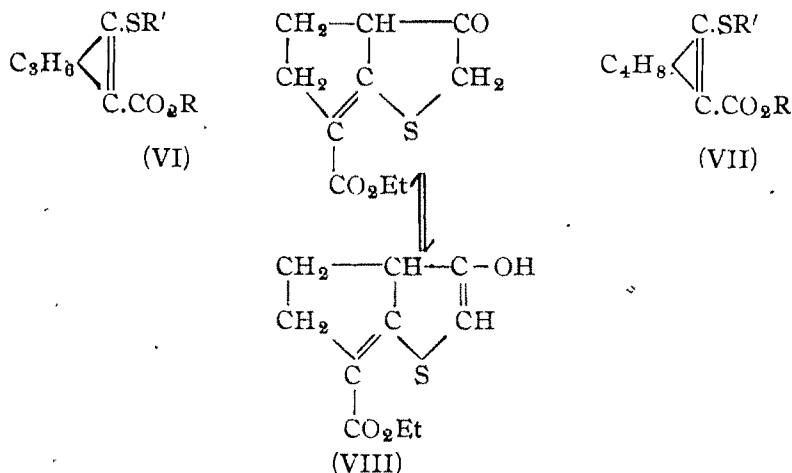
It is interesting to note that somewhat different route is chosen by β -thiocyclopentanone carboxylic ester in the reaction. The hydroxy compound, previously described, instead of undergoing internal lactonisation reacts with another molecule of the ester in thiol-phase to give rise to a sulphide (IVa).



This is in agreement with what has been foretalled that the thiolised ester primarily adds to the carbonyl group giving rise to hydroxy sulphide.

α -Halogenated fatty esters have been condensed with the keto esters. The resulting products have been cyclised to give rise to thiophene bodies (VIII). Thiocyclohexanone carboxylic ester under this condition furnishes hexahydrothionaphthene (Va). Thio-thiol has been estimated by the iodometric method (Mitra, *J. Indian Chem. Soc.* 1938, 15, 205).





EXPERIMENTAL.

Preparation of Thio-ester.—The cyclic keto-ester was dissolved in ethyl alcohol (10 g. in 40 c.c.), saturated with dry hydrogen chloride at 0° , and hydrogen sulphide was passed (24 hours) through the solution standing over ice, the oil that separated was extracted with benzene. The benzene solution was washed with dilute sodium carbonate, and dried over anhydrous sodium sulphate. The benzene was removed, and the residual oil distilled under reduced pressure. The following compounds were thus prepared: *ethyl thiocyclopentan-1-one-2-carboxylate*, b. p. $110^\circ/5.5$ mm. (Found: C, 56.0; H, 7.3; S, 18.2. $\text{C}_8\text{H}_{12}\text{O}_2\text{S}$ requires C, 55.8; H, 6.9; S, 18.6 per cent). *Ethyl thiocyclohexan-1-one-2-carboxylate*, b. p. $112^\circ/6$ mm. (Found: C, 57.9; H, 7.36. $\text{C}_9\text{H}_{14}\text{O}_2\text{S}$ requires C, 58.07; H, 7.52 per cent).

Hydrolysis of Thio-esters.—When the above thio-esters (5-10 g.) were refluxed (4-6 hours) with 10% barium hydroxide (100 c.c.), only a small amount of the corresponding thio-acids was isolated. The yield was, however, considerably increased by the following process.

The thio-ester (2.25 g.) was taken in alcoholic sodium hydroxide (25 c.c. of 33%), and the mixture immediately heated on a water-bath (20 minutes). It was then quickly cooled over ice, the mixture acidified with dilute hydrochloric acid in the cold, rapidly filtered, and dried at 60° cautiously under suction. The crude acid was crystallised from a mixture of dry ether and petroleum ether (b.p. $80^\circ-90^\circ$) giving glistening flakes (yield 60%). Following acids were isolated:—*Thiocyclopentan-1-one-2-carboxylic acid*, m. p. 122° (decomp.). (Found: S, 21.9. $\text{C}_6\text{H}_8\text{O}_2\text{S}$ requires S, 22.2 per cent). *Thiocyclohexan-1-one-2-carboxylic acid*, m. p. 115° (decomp.). (Found: C, 52.9; H, 6.6. $\text{C}_7\text{H}_{10}\text{O}_2\text{S}$ requires C, 53.2; H, 6.3 per cent).

Preparation of Alkyl and other Derivatives.—The thio-ester in sodium-dried benzene was slowly added to emulsified sodium, suspended in dry benzene at 0° . When the reaction had abated, the mixture was left (8 hours) at the room temperature (25°). Alkyl halides were then added and the mixture refluxed (6 hours). The product was cooled and treated with excess of water containing a few c.c. of hydrochloric acid and the benzene layer was collected and dried. The benzene was removed and the residual oil distilled. Following compounds were prepared :

Ethyl 1-ethylmercaptocyclopentene-2-carboxylate (VI, $R=R'=Et$), b.p. $115^{\circ}/6$ mm., from ethyl thiocyclopentanone-2-carboxylate (9 g.), ethyl iodide (32 g.), and emulsified sodium (1 g.). (Found : S, 15.6. $C_{10}H_{18}O_2S$ requires S, 16.0 per cent). *Ethyl 1-methylcarbethoxymercaptocyclopentene-2-carboxylate*, (VI, $R=Et$; $R'=CH_2CO_2Et$), b.p. $170^{\circ}/3$ mm., from thiocyclopentanone 2-carboxylate (10 g.), ethyl monochloroacetate (19 g.) and emulsified sodium (1.5 g.). (Found : S, 12.7. $C_{12}H_{18}O_4S$ requires S, 12.4 per cent). *Ethyl 1-ethylmercaptocyclohexene-2-carboxylate*, (VII; $R=R'=Et$), b.p. $125^{\circ}/3$ mm., from ethyl thiocyclohexanone-2-carboxylate (11 g.), ethyl iodide (23 g.) and molecular sodium (1.8 g.). (Found : C, 61.4; H, 8.56. $C_{11}H_{18}O_2S$ requires C, 61.6; H, 8.4 per cent). *Ethyl 1-acetylmercaptocyclohexene-2-carboxylate*, (VII, $R=Et$; $R'=CO\cdot Me$), b.p. $132^{\circ}/5$ mm., from thiocyclohexanone-2-carboxylate (10 g.), acetylchloride (5 g.) and molecular sodium (1.1 g.). (Found : C, 57.8; H, 7.1; S, 13.5. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.0; S, 14.0 per cent).

Hydrolysis of the above Alkyl Derivatives.—The thio-esters (VI & VII) were dissolved in alcoholic sodium hydroxide (10 c.c.) in the cold and kept at room temperature for 8-10 hours. The mixture was cooled in ice and acidified with dilute hydrochloric acid in the cold. The solid which separated was dissolved in sodium bicarbonate and liberated by dilute mineral acid, and crystallised from acetic acid (charcoal). The following compounds were obtained :

1-Ethylmercaptocyclopentene-2-carboxylic acid, (VI, $R=H$; $R'=Et$), m.p. 177° , from thio-ether (VI, $R=R'=Et$, 5 g.) and sodium hydroxide (1.4 g.). (Found : C, 55.6; H, 6.9; S, 18.4. $C_8H_{12}O_2S$ requires C, 55.8; H, 6.9; S, 18.6 per cent). *1-Ethylmercaptocyclohexene-2-carboxylic acid*, (VII, $R=H$, $R'=Et$), m.p. 146° from thio-ether (VIII, $R=R'=Et$, 5 g.) and sodium hydroxide (2 g.). (Found : C, 57.9; H, 7.4. $C_9H_{14}O_2S$ requires C, 58.0; H, 7.5 per cent).

The thio-ether (VI, $R=Et$, $R'=CH_2CO_2Et$, 9 g.) was gradually added to molecular sodium (1.8 g.) suspended in dry benzene (150 c.c.). It was

then left at the room temperature (25°) overnight. The sodium salt thus precipitated was washed with a few c.c. of benzene. This was then decomposed by dilute hydrochloric acid in the cold, and was extracted with further quantity of benzene, dried, and benzene distilled away. The residual oil, thus left, was distilled, b.p. 140°/5 mm. This on keeping solidified to greenish needles, m.p. 54°. (Found: S, 15.6. $C_{10}H_{12}O_3S$ requires S, 15.1 per cent). This gives an indophenin reaction with isatin in the presence of concentrated sulphuric acid and gives a phenolic colour with ferric chloride (VIII).

3-Oxy-7-carbethoxy-4:6-dihydrothionaphthene (Va).—To a suspension of emulsified sodium (1.2 g.) in sodium-dried benzene (50 c.c.) cyclohexanone-2-carboxylate (15 g.) was slowly added in the cold. After the completion of the reaction, it was left at room temperature (25°) for 8 hours. Ethyl monochloroacetate (8 g.) was then added and the mixture was refluxed (16 hours). On cooling it was then treated with excess of water containing a few c.c. of hydrochloric acid and was extracted with further quantity of benzene, the benzene dried, and removed. The residual oil was distilled at 150°-52°/4.5 mm., which solidified on keeping to thick elongated plates, m.p. 59°. (Found: S, 14.1. $C_{11}H_{14}O_3S$ requires S, 14.2 per cent).

Condensation of Aldehydes with Thio-acids or Thio-esters, (VI & VII, R=H; R'=H or Et).—The thio-acids or thio-esters were dissolved in alcohol (5 c.c.) saturated with dry hydrogen chloride at 0° and mixed with aldehydes in equimolecular proportions, and allowed to stand over ice (1 hour). The solid separating was collected, washed with ice-water and crystallised from acetic acid or alcohol. The following compounds were prepared from thio-acids (VI, R=R'=H):—

Di-(1-carboxy- Δ^1 -thiocyclopentenyl)-p-methoxyphenylmethane (IVa, R=H; R'=C₆H₄OMe), m.p. 185° (decomp.), from thio-acid (1 g.), and anisaldehyde (1 g.). (Found: S, 15.3. $C_{20}H_{22}O_6S_2$ requires S, 15.7 per cent). *Di-(1-carboxy- Δ^1 -thiocyclopentenyl)-phenylmethane (IVa, R=H; R'=Ph),* m.p. 221° (decomp.), from thio-acid (1 g.) and benzaldehyde (1 g.). (Found: S, 17.1. $C_{16}H_{20}O_4S_2$ requires S, 17.0 per cent). *Di-(1-carboxy- Δ^1 -thiocyclopentenyl) cinnamylidinemethane, (IVa, R=H; R'=CH=CHPh),* m.p. 127°, from thio-acid (1 g.) and cinnamic aldehyde (5 g.). (Found: S, 15.3. $C_{30}H_{32}O_6S_2$ requires S, 15.7 per cent).

The following compounds were obtained from thio-ester (VI, R=H; R'=Et): *Di-(1-carbethoxy- Δ^1 -thiocyclopentenyl)-p-methoxyphenylmethane, (IVa, R=Et; R'=C₆H₄OMe),* m.p. 118°, from thio-ester (1 g.) and anisaldehyde (1 g.). (Found: C, 61.9; H, 6.6; S, 14.1. $C_{24}H_{30}O_6S_2$ requires C, 62.3; H, 6.4; S, 13.9 per cent). *Di-(1-carbethoxy- Δ^1 -thio-*

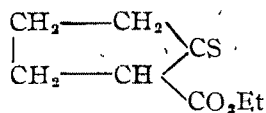
cyclopentenyl)-4-hydroxy-3-methoxyphenylmethane, [IVa, R=Et; R'=C₆H₃(OH)(OMe)], m.p. 136°, from thio-ester (1.3 g.) and vanillin (1 g.). (Found: C, 59.9; H, 6.5. C₂₄H₃₀O₆S₂ requires C, 60.2; H, 6.3 per cent). Di-(1-carbethoxythiocyclopentenyl)-phenylmethane (IVa, R=Et; R'=Ph), m.p. 140°, from benzaldehyde (1 g.) and thio-ester (1 g.). (Found: C, 63.64; H, 6.4. C₂₃H₂₈O₄S₂ requires C, 63.88; H, 6.7 per cent). The molecular weight of this compound was determined by freezing point method in benzene solution. (Found: M.W., 424. C₂₃H₂₈O₄S₂ requires M.W., 430). The corresponding simple methane analogue, m.p. 117° (IVa, R=Et; R'=H), from formaldehyde (2 c.c. of 40% aq. soln.) and thio-ester (1 g.) (Found: S, 17.6. C₁₇H₂₄O₄S₂ requires S, 18.0 per cent).

The following compounds were prepared from the thio-acid (VII, R=R'=H): α -Keto- β - γ -tetramethylene- μ phenyl-thioxine, (III, R=Ph), m.p. 85°, from benzaldehyde (1 g.) and thio-acid (1 g.) (Found: C, 67.9; H, 5.9. C₁₄H₁₄O₂S requires C, 68.2; H, 5.7 per cent). The corresponding 2-(3'-methoxy-4'-hydroxy)-phenyl analogue (III, R=HO. C₆H₃(OMe)), m.p. 178° from vanillin (1 g.) and thio-acid (1 g.). (Found: C, 61.5; H, 5.4. C₁₅H₁₆O₄S requires C, 61.6; H, 5.5 per cent). The 2-(3'-methoxyphenyl) analogue, (III, R=C₆H₄(OMe)), m.p. 124°, from thio-acid (1 g.) and anisaldehyde (0.5 g.). (Found: C, 65.3; H, 6.0. C₁₈H₁₈O₃S requires C, 65.2; H, 5.8 per cent).

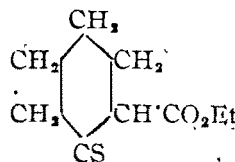
Benzaldehyde was similarly condensed with thio-ester (VII, R=Et; R'=H). The product obtained was found to be identical with the compound obtained from the thioketo-acid and benzaldehyde.

Thio-thiol Estimation.—The results of the estimation of the two tautomeric forms of the thioketo-esters are given below.

TABLE I.



(A)



(B)

| Solvent | Temp | A. Thiol | B. Thiol |
|---------|------|-------------|-------------|
| EtOH | 30° | 36.6% | 77.4% |
| EtOH | 60° | 35.1 | 75.7 |

Our thanks are due to Sir P. C. Rây for his kind interest in this work.

THE EFFECT OF PHENYL GROUP ON THE ROTATORY POWER : PHENYLCAMPHORANILIC ACIDS AND *p*-IMINO-*d*-CAMPHORDIPHENYL.

BY MAHAN SINGH AND ARJAN SINGH.

2'-, *3'*- and *4'*-phenylcamphoranilic acids and *p*-imino-*d*-camphordiphenyl have been prepared and the rotatory powers observed at the full neutralisation point.

It is now well established that the polar effect of a substituent group is manifest in optical activity. The order in which the substituents are arranged is identical with the order obtained from the dipole moment and the dissociation constant of the acid (Ruie, *J. Chem. Soc.*, 1924, 125, 1121, and subsequent papers). The electron attractive or electron repulsive nature of groups is identified with the amount of restraint exercised by the groups over their co-valency electrons and the common substituents give the following diminished order : COOH, NO₂, Halogens, OH, C₆H₅, H, alkyl.

Singh and Singh (*J. Indian Chem. Soc.*, 1940, 17, 486) have, however, shown that the position of the CN group in the sequence of substituent groups is anomalous. We have now prepared phenylcamphoranilic acids. *4'*-Phenylcamphoranilic acid has $[\alpha]_D = 64^\circ$ which is next to *4'*-carboxylcamphoranilic acid in the series which represent a gradual transition from strongly electronegative groups through hydrogen to those increasingly electropositive in character. The values of the *4'*-acids in methyl alcohol are given below.

| COOH | Ph | Et | Cl | CN | OBt | Me | OMe | Br | I |
|------|----|----|------|----|------|----|------|------|----|
| 255 | 64 | 59 | 58.8 | 58 | 56.3 | 56 | 53.3 | 51.3 | 44 |

The phenyl group, which falls after the carboxyl, should be down below the series.

The effect of phenyl group in the *3'* position is equally curious and is not easy to explain. The values of the *3'*-acids in methyl alcohol are tabulated below.

| COOH | Cl | F | OBt | OMe | CN | Br | NO ₂ | I | Ph |
|------|------|------|-----|------|------|------|-----------------|-------|------|
| 146 | 52.5 | 52.4 | 50 | 49.7 | 48.4 | 44.3 | 43.2 | 41.69 | 40.8 |

It was expected that the phenyl group would be high up in the series, but it occupies the extreme end position. In methylethyl ketone, *3'*-phenyl-

camphoranilic acid gives negative rotation $[\alpha]_D = -7.5^\circ$, a behaviour hitherto not shown by any other group in the *meta* position.

The behaviour of the phenyl group is, however, quite normal in the 2' position. It gives low rotation in methyl and ethyl alcohols and acetone and the sign is reversed in methyl ethyl ketone.

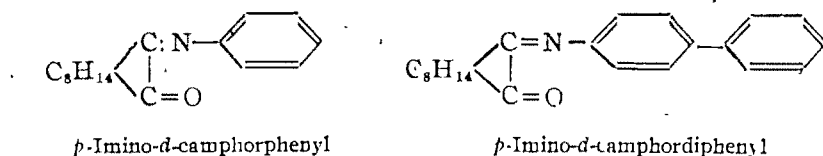
Rupe and Wolfsleben (*Annalen*, 1912, 396, 135) have studied the effect of the phenyl group on rotatory power. They also have come to the conclusion that close to the asymmetric C-atom the phenyl group nearly always increases the optical rotation, but in general its effect is curious.

The rotatory powers of all the three acids were determined at the full neutralisation point and in every case there is an increase (*vide* experimental).

We have also prepared *p*-imino-*d*-camphordiphenyl by condensing camphorquinone with *p*-aminodiphenyl and have determined its rotatory powers in various solvents. These values and those of phenyliminocamphor are given below.

| | MeOH | EtOH | C ₆ H ₆ | CHCl ₃ | C ₆ H ₅ N |
|--|-------|-------|-------------------------------|-------------------|---------------------------------|
| <i>p</i> -Imino- <i>d</i> -camphorphenyl | 606.8 | ... | ... | 726.0 | ... |
| <i>p</i> -Imino- <i>d</i> -camphordiphenyl | 696.8 | 720.7 | 775 | 780 | 782 |

There is thus a small increase in the rotatory power by the introduction of the phenyl group. It was, however, expected that with the length of the conjugated system, the increase would be much greater. The formulae of the two are given for the sake of comparison.



p-Imino-*d*-camphordiphenyl was reduced by shaking the ethereal solution with zinc and 10% potassium hydroxide. Diphenylaminocamphor crystallised as white leaf crystals, $[\alpha]_D = 82.3^\circ$ (ethyl alcohol). This was expected as the conjugation is broken.

EXPERIMENTAL.

Camphoric anhydride and aminodiphenyls in molecular proportions were heated with a little fused sodium acetate for 3 to 4 hours in an oil-bath at 130-135° in the case of *para* and at 120° in the case of *ortho* and *meta*. The product was extracted with dilute ammonium hydroxide solution and

the filtrate was acidified with dilute hydrochloric acid. The solid mass was crystallised from alcohol (animal charcoal).

2'-Phenylcamphoranilic acid crystallised from alcohol as white crystalline product, m.p. 181° . It is readily soluble in methyl alcohol, ethyl alcohol, acetone and methylethyl ketone. (Found: N, 4.27; Equiv., 351. $C_{22}H_{25}O_3N$ requires N, 3.98 per cent. Equiv., 351).

3'-Phenylcamphoranilic acid was obtained as crystalline powder with a faint pinkish tinge, m.p. 204.5° . (Found: N, 4.18; Equiv., 349. $C_{22}H_{25}O_3N$ requires N, 3.98 per cent. Equiv., 351).

4'-Phenylcamphoranilic acid was obtained as white amorphous powder, m.p. $196-97^{\circ}$ after shrinking at 194° . (Found: N, 4.17; Equiv., 353. $C_{22}H_{25}O_3N$ requires N, 3.98 per cent. Equiv., 351).

Equimolecular quantities of *p*-aminodiphenyl and camphorquinone with anhydrous sodium sulphate as a condensing agent, were heated for 3 hours on a water-bath. After cooling, the condensed product was poured into water. The dark brown colouring matter was removed after repeated crystallisations from dilute alcohol and treatment with animal charcoal whereby beautiful yellow crystals were obtained, m.p. $148-49^{\circ}$. (Found: N, 4.4. $C_{22}H_{23}ON$ requires N, 4.4 per cent). It is readily soluble in common organic solvents.

TABLE I.

Rotation of phenylcamphoranilic acids.

| Solvent. | 2'-Phenyl acid. | | | 3'-Phenyl acid. | | | 4'-Phenyl acid | | |
|--------------------------------|-----------------------|--------------|---------------------|-----------------------|--------------|---------------------|-----------------------|--------------|---------------------|
| | Conc. (g./25 c.c.) | α_D . | $[\alpha]_D^{20}$. | Conc. (g./25 c.c.) | α_D . | $[\alpha]_D^{20}$. | Conc. (g./25 c.c.) | α_D . | $[\alpha]_D^{20}$. |
| MeOH | 0.2500 | 0.53 | 26.5 | 0.1500 | 0.49 | 40.8 | 0.2500 | 1.28 | 64.0 |
| EtOH | 0.2500 | 0.46 | 23.0 | 0.1500 | 0.30 | 25.0 | 0.2500 | 1.10 | 55.0 |
| Me ₂ CO | 0.2500 | 0.14 | 7.0 | 0.1500 | 0.23 | 19.6 | ... | ... | ... |
| MeEtCO | 0.2500 | -0.12 | -6.0 | 0.1500 | -0.09 | -7.5 | ... | ... | ... |
| CHCl ₃ | ... | ... | .. | ... | ... | .. | 0.1500 | 0.51 | 42.5 |
| After full neutralisation with | | | | | | | | | |
| NaOH | 0.1755 | 0.50 | 35.6 | 0.2500 | 1.10 | 55.0 | 0.1755 | 1.05 | 74.7 |

TABLE II.

p-Imino-*d*-camphordiphenyl.

| Conc. (g./25 c.c.) = 0.1200 | | | | | |
|-----------------------------|------------|-------------------------|-------------------|------------|-------------------------|
| Solvents. | α_D | $[\alpha]_D^{20^\circ}$ | Solvents. | α_D | $[\alpha]_D^{20^\circ}$ |
| EtOH | 6.92 | 720.7 | MeEtCO | 6.83 | 711.4 |
| MeOH | 6.69 | 696.8 | Benzene | 7.44 | 775.0 |
| Me ₂ CO | 6.75 | 703.1 | CHCl ₃ | 7.49 | 780.2 |
| | | | Pyridine | 7.51 | 782.1 |

p-Amino-*d*-camphordiphenyl.

| Conc. (g./25 c.c.) = 0.1200 | | |
|-------------------------------|------------|-------------------------|
| Solvents. | α_D | $[\alpha]_D^{20^\circ}$ |
| EtOH | 7.9 | 82.3 |
| MeEtCO | 8.9 | 92.7 |
| C ₆ H ₆ | 9.6 | 100.0 |

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PARACHOR OF THYMOL, MENTHOL AND *p*-TOLUIDINE IN DIFFERENT SOLUTIONS.

BY S. S. DESHAPANDE, S. N. KAWRSESHWAR AND W. V. BHAGWAT.

Parachor of thymol, menthol and *p*-toluidine in nitrobenzene, acetic acid etc. has been determined at different concentrations. It is observed that the values of parachor at temperatures, where these substances exist as liquid and at temperatures where they exit as solids, are practically the same as obtained by solution methods. The Hammick and Andrew's equation, therefore, is applicable both in liquid and solid states for the solutes. The nature of the solvent does not seem to have any appreciable effect on the values of the parachor of solutes. At lower concentrations of the solute the values obtained by Hammick and Andrew's equation show greater variation from the calculated values.

The method employed for determining the parachor in solution is the same as that due to Hammick and Andrew (*J. Chem. Soc.*, 1929, 755). Thus

$$P_{\text{M}} = P(1-x) + P_{\text{X}}x \quad \dots (i)$$

$$P_{\text{X}} = \frac{M_{\text{X}}}{(D-d)}\gamma^{\frac{1}{4}} \quad \dots (ii)$$

$$\text{and} \quad M_{\text{M}} = M_{\text{S}} (1-x) + M_{\text{X}}x \quad \dots (iii)$$

Where P_{M} = parachor of the mixture, P_{X} = the parachor of the solute, P = the parachor of the solvent, x = the molar fraction of the solute, $(1-x)$ = the molar fraction of the solvent, M_{X} = the mean molecular weight, D = the density of the solution, γ = surface tension of the solution, M_{S} = the molecular weight of the solvent and M_{X} = the molecular weight of the solute.

The value of γ was determined by Jaeger's bubble method. The value of D was found by pycnometer, while the value of d , the density of the vapour of the solvent was neglected. The value of g substituted is 978 dynes/cm. cm. at Indore.

Thymol melts at 50°. It will be observed from the table below that the values determined by keeping the solution below, above and at the melting point of thymol, differ only very slightly. In general it is observed that as the concentration of the solute is decreased the values obtained by Hammick and Andrew's formula deviate more and more from the calculated value (377 for thymol). Temperature seems to have no effect on the value of the parachor.

TABLE I.

Parachor of thymol in nitrobenzene.

| $x=0.176.$ | | | | | $x=0.229.$ | | | | |
|------------|----------|-----------|-------|-------|------------|-----------|-----------|-------|-------|
| Temp. | Density. | $\gamma.$ | P_M | P_X | Temp. | Density | $\gamma.$ | P_M | P_X |
| 40° | 1.137 | 36.16 | 274.8 | 373 | 20° | 1.137 | 38.7 | 282.6 | 375 |
| 45 | 1.130 | 35.9 | 275.8 | 373 | 30 | 1.129 | 37.5 | 283.3 | 378 |
| 50 | 1.126 | 35.5 | 276.2 | 376 | 40 | 1.12 | 37.4 | 285.2 | 386 |
| 55 | 1.121 | 34.6 | 275.4 | 371 | 50 | 1.111 | 35.6 | 284.5 | 383 |
| 60 | 1.118 | 34.8 | 276.4 | 377 | 60 | 1.105 | 34.2 | 282.8 | 377 |
| $x=0.122.$ | | | | | $x=0.095.$ | | | | |
| Temp. | Density. | $\gamma.$ | P_M | P_X | Density | $\gamma.$ | P_M | P_X | |
| 20° | 1.166 | 40.9 | 273.9 | 401 | 1.177 | 39.55 | 268.0 | 392 | |
| 30 | 1.157 | 39.7 | 274.1 | 402 | 1.169 | 38.72 | 267.8 | 389 | |
| 40 | 1.148 | 37.7 | 271.9 | 393 | 1.158 | 37.08 | 267.4 | 386 | |
| 50 | 1.141 | 36.1 | 271.3 | 388 | 1.148 | 36.26 | 268.4 | 396 | |
| 60 | 1.131 | 35.2 | 272.2 | 392 | 1.137 | 34.55 | 267.3 | 385 | |
| 70 | 1.123 | 34.0 | 271.6 | 391 | 1.132 | 33.7 | 267.2 | 382 | |
| $x=0.214$ | | | | | | | | | |
| Temp. | Density. | $\gamma.$ | P_M | P_X | | | | | |
| 20° | 1.142 | 37.55 | 279.9 | 370 | | | | | |
| 30 | 1.132 | 35.83 | 278.7 | 368 | | | | | |
| 40 | 1.122 | 35.20 | 279.6 | 371 | | | | | |
| 50 | 1.115 | 34.34 | 279.0 | 369 | | | | | |
| 60 | 1.107 | 33.59 | 280.3 | 375 | | | | | |
| 70 | 1.099 | 32.84 | 280.5 | 376 | | | | | |

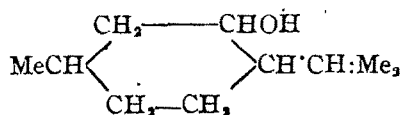
TABLE II.

Parachor of thymol in acetic acid.

| $x=0.176. P_{calc}=377.0$ | | | | |
|---------------------------|----------|-----------|-------|-------|
| Temp. | Density. | $\gamma.$ | P_M | P_X |
| 20° | 1.022 | 29.1 | 174.8 | 379 |
| 30 | 1.014 | 27.28 | 169.4 | 349 |
| 40 | 1.004 | 26.64 | 174.1 | 375 |
| 50 | 0.9942 | 25.89 | 174.5 | 377 |
| 60 | 0.9855 | 25.14 | 174.8 | 379 |
| 70 | 0.9776 | 24.39 | 175.0 | 380 |

The values are very good showing that, as in the case of liquid-liquid mixture, where only one liquid is associating, there is no effect on the value of parachor, in the case of solid-liquid solution also, where the liquid is associating, the value of parachor is not affected.

Determination of Parachor of Menthol.—The following structure for menthol is assumed :



PARACHOR OF THYMOL, MENTHOL AND *p*-TOLUIDINE, ETC. 151

TABLE III.
Solvent—Nitrobenzene.

| $x=0.081.$ | | | | | $x=0.198.$ | | | |
|------------|----------|------------|---------|---------|------------|------------|---------|---------|
| Temp. | Density. | γ . | P_M . | P_X . | Density | γ . | P_M . | P_X . |
| 20° | 1.165 | 36.0 | 265.3 | 383 | | | | |
| 30 | 1.158 | 34.8 | 263.2 | 361 | | | | |
| 40 | 1.149 | 33.59 | 263.1 | 360 | 1.096 | 31.48 | 280.0 | 381 |
| 50 | 1.140 | 32.3 | 262.6 | 354 | 1.088 | 30.68 | 280.0 | 381 |
| 60 | 1.132 | 31.56 | 263.1 | 360 | 1.077 | 28.96 | 278.6 | 375 |
| 70 | ... | ... | ... | ... | 1.069 | 28.22 | 279.6 | 379 |

| $x=0.238.$ | | | | | $x=0.255.$ | | | |
|------------|----------|------------|---------|---------|------------|------------|---------|---------|
| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . |
| 20° | 1.100 | 32.96 | 286.8 | 389 | 1.094 | 33.70 | 289.5 | 393 |
| 30 | 1.091 | 32.28 | 287.6 | 392 | 1.084 | 32.95 | 290.6 | 395 |
| 40 | 1.083 | 31.45 | 287.6 | 392 | 1.076 | 32.31 | 291.1 | 396 |
| 50 | 1.074 | 30.81 | 288.7 | 396 | 1.066 | 31.67 | 292.3 | 401 |
| 60 | 1.064 | 31.13 | 292.1 | 411* | 1.057 | 30.92 | 293.1 | 405 |
| 70 | 1.057 | 29.85 | 290.1 | 403 | 1.049 | 30.16 | 293.6 | 406 |

| $x=0.084.$ | | | | | $x=0.173.$ | | | |
|------------|----------|------------|---------|---------|------------|------------|---------|---------|
| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . |
| 20° | 1.017 | 25.67 | 150.7 | 373 | 0.9906 | 28.14 | 178.1 | 401 |
| 30 | 1.206 | 24.88 | 151.1 | 378 | 0.9822 | 26.43 | 176.9 | 394 |
| 40 | 0.9961 | 23.11 | 149.5 | 359* | 0.9736 | 26.74 | 178.9 | 406 |
| 50 | 0.9858 | 22.57 | 150.5 | 370 | 0.9641 | 24.93 | 177.5 | 398 |
| 60 | 0.9757 | 21.82 | 149.2 | 355* | 0.9532 | 23.32 | 176.7 | 393 |
| 70 | 0.9650 | 21.18 | 151.3 | 379 | 0.9446 | 23.00 | 177.6 | 399 |
| 80 | 0.9532 | 20.36 | 151.8 | 386 | ... | ... | ... | ... |

TABLE IV.

Parachor of menthol in carbon tetrachloride.

| | Temp. | Density | γ | P_M . | P_X . |
|-----------|----------------|---------|----------|----------------|---------|
| $x=0.161$ | 20° | 1.412 | 30.81 | 254.2 | 438 |
| | 30 | 1.396 | 29.25 | 253.9 | 436 |
| | 40 | 1.384 | 27.00 | 252.0 | 424 |
| | Menthol liquid | | | | |
| | 60 | 0.856 | 27.17 | | 416.1 |
| | | | | Calc. parachor | 416.1 |

This value is identical with the value calculated for the formula. Calculated value for the parachor of menthol is 416.1. The results, therefore, are low as given by Hammick and Andrew's formulae and more so, if the concentration of the solute is low. In carbon tetrachloride, however, the values are high.

Parachor of *p*-toluidine in nitrobenzene.

TABLE V.

| $x=0.267$ | | | | | $x=0.313^c$ | | | | |
|-----------|----------|------------|---------|---------|-------------|------------|---------|---------|--|
| Temp | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . | |
| 20° | 1.128 | 40.98 | 270.5 | 278 | 1.136 | 41.73 | 264.1 | 284 | |
| 30 | 1.122 | 40.12 | 269.1 | 274 | 1.127 | 39.90 | 263.4 | 282 | |
| 40 | 1.114 | 39.37 | 271.1 | 280 | 1.117 | 38.08 | 262.5 | 279 | |
| 50 | 1.106 | 37.55 | 270.1 | 277 | 1.109 | 36.38 | 261.3 | 275 | |
| 60 | 1.097 | 36.27 | 269.7 | 276 | 1.100 | 35.63 | 262.0 | 277 | |
| 70 | 1.087 | 35.62 | 270.0 | 277 | 1.091 | 34.87 | 262.6 | 279 | |
| $x=0.403$ | | | | | $x=0.214$ | | | | |
| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . | |
| 20° | 1.109 | 40.12 | 264.5 | 279 | 1.152 | 37.34 | 256.0 | 264 | |
| 30 | 1.106 | 39.15 | 263.6 | 278 | 1.142 | 36.59 | 257.6 | 268 | |
| 40 | 1.097 | 38.41 | 265.0 | 280 | 1.133 | 35.94 | 258.3 | 271 | |
| 50 | 1.087 | 36.71 | 263.4 | 275.9 | 1.124 | 35.21 | 259.1 | 274 | |
| 60 | 1.080 | 35.83 | 264.3 | 277 | 1.115 | 34.55 | 260.1 | 278 | |
| 70 | 1.070 | 35.20 | 265.1 | 280 | 1.107 | 33.70 | 259.2 | 275 | |
| $x=0.467$ | | | | | $x=0.122$ | | | | |
| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . | |
| 20° | 1.100 | 42.58 | 266.2 | 279 | 1.179 | 41.61 | 260.7 | 301 | |
| 30 | 1.092 | 40.76 | 266.2 | 279 | 1.169 | 40.87 | 261.5 | 306 | |
| 40 | 1.084 | 39.90 | 266.8 | 280 | 1.161 | 40.12 | 262.3 | 315 | |
| 50 | 1.076 | 39.15 | 268.0 | 283 | 1.152 | 38.94 | 262.5 | 316 | |
| 60 | 1.064 | 37.54 | 268.4 | 284 | 1.143 | 37.12 | 261.3 | 305 | |
| 70 | 1.057 | 36.81 | 268.8 | 285 | 1.133 | 34.63 | 258.9 | 287 | |
| $x=0.091$ | | | | | | | | | |
| Temp. | Density. | γ . | P_M . | P_X . | | | | | |
| 20° | 1.184 | | 43.0 | 262.8 | | | | | |
| 30 | 1.174 | | 41.3 | 262.2 | | | | | |
| 40 | 1.165 | | 39.48 | 261.3 | | | | | |
| 50 | 1.157 | | 37.65 | 260.1 | | | | | |
| 60 | 1.149 | | 36.91 | 260.5 | | | | | |
| 70 | 1.139 | | 35.20 | 259.9 | | | | | |

The calculated value for the parachor of *p*-toluidine is 275.9. The experimental agreement is excellent at higher concentrations.

PARACHOR OF SOME ORGANIC COMPOUNDS AND THEIR CHEMICAL CONSTITUTIONS.

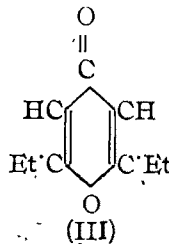
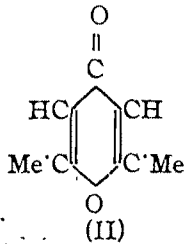
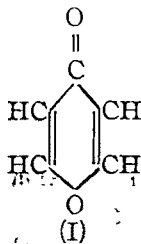
By S. S. DESHAPANDE, S. N. KAWERSHWAR AND W. V. BHAGWAT.

Parachor of simple pyrone, dimethyl and diethylpyrones have been determined in ethyl acetate and nitrobenzene. The value in case of pyrone and diethylpyrone approaches more to the simple ring formulae and therefore must have the structure suggested by Deshapande (*J. Indian Chem. Soc.*, 1932, 9, 303), while dimethylpyrone should be represented by Collie's bridge-ring structure

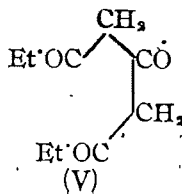
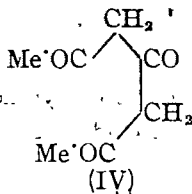
The structure of diacetylacetone has also been investigated. Its value of parachor in ethyl acetate approaches Collie's bridge-formulae.

The calculation of parachor for bridge-ring is carried on the basis that a bridge-ring is made of two rings each of five atoms and this finds justification from the authors' observations on *isonitrosocampor* which is known to contain bridge-ring. The value of its parachor in nitrobenzene is the same as calculated on the basis of the above assumption for the bridge-ring.

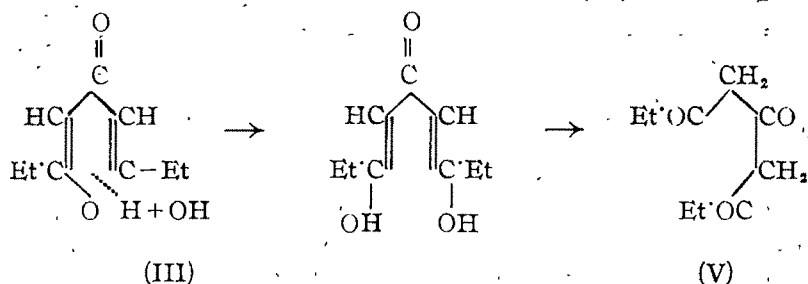
In our previous paper (*This Issue*, p. 149) we have shown from the results obtained with the low melting substances that, working under certain conditions, the parachor of a solid substance obtained from its solution is almost identical with that of the same substance worked above its melting point without any solvent; and these values are in turn identical with the calculated values corresponding to its accepted formula. We have now made use of this important observation in the case of certain organic compounds about whose structures two opinions have been held on chemical evidence. These compounds are the pyrone (I) and its dimethyl (II) and diethyl (III) derivatives and the 1:3:5 triketones related to the pyrones.



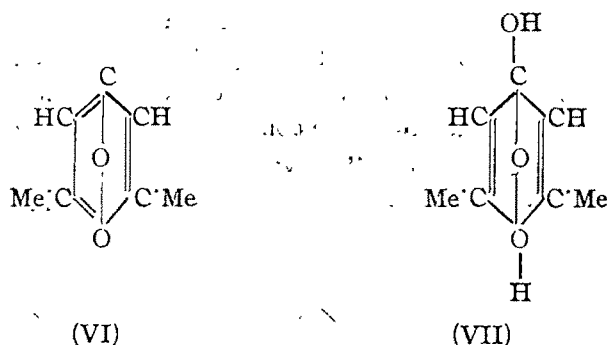
On fusion by means of baryta the dimethyl and diethylpyrones give diacetylacetone (IV) and the dipropionylacetone (V) respectively.



Structures (IV) and (V) have been established on chemical grounds by Deshapande, Dingankar and Kokil (*J. Indian Chem. Soc.* 1934, 11, 595) and as (IV) and (V) result from (II) and (III) (Deshapande, *ibid.*, 1932, 9, 303), the structures of the latter should be by inference what they are shown to be



Collie, however, on the ground that the pyrones form substitution products instead of addition products in spite of their containing two double bonds in the ring, thought that they are aromatic compounds, and must therefore contain three alternate double bonds in the ring. He therefore, assigned structure (VI) to dimethylpyrone and (VII) to diacetylacetone.



Parachor method has been used to ascertain whether the simple ring structure of pyrones by Deshapande (*loc. cit.*) or bridge-ring structure proposed by Collie is the correct one. Diethylpyrone (III) was chosen it being a liquid and therefore it was possible to obtain its parachor both in pure condition as well as in solution (Table I). The diethylpyrone was purified by distillation under reduced pressure. Parachor calc. for (III) is 359.1 and that for Collie's formula is 370.

The following results were obtained for diethylpyrone dissolved in ethyl acetate. Parachor of the pure solvent was found to be 215.5 while with the formula it comes to 216.

TABLE I.

Diethylpyrone.

| $\alpha=0.203.$ | | | | | |
|-----------------|----------|------------|---------|---------|--|
| Temp. | Density. | γ . | P_M . | P_X . | |
| 20° | 0.9446 | 26.20 | 241.8 | 355 | |
| 30 | 0.9336 | 25.39 | 242.7 | 359.5 | |
| 40 | 0.9244 | 24.59 | 243.0 | 361 | |
| 50 | 0.9153 | 23.63 | 243.3 | 362 | |
| 60 | 0.9060 | 22.68 | 243.3 | 362 | |

In the homologous series of pyrones there seems to be something unusual. The first member, the simple pyrone (I), is a solid melting at 32° and boiling at 215° at ordinary pressure. The next member, dimethylpyrone (II) is a high melting solid, m. p. 132°; but the next member, diethylpyrone (III), is a liquid, b. p. 115°-120°/10 mm. Chemical methods fail to explain this anomaly and it was thought interesting to apply the parachor method so as to throw any light on the structure of these substances.

The following results were obtained with pyrone (I) which was purified by two distillations, and was dissolved in ethyl acetate. Parachor calculated is 208.1 by simple ring formula.

TABLE II.

Pyrone.

| Temp. | Density. | $\alpha=0.129.$ | | | Density. | $\alpha=0.262.$ | | |
|-------|----------|-----------------|---------|---------|----------|-----------------|---------|---------|
| | | γ . | P_M . | P_X . | | γ . | P_M . | P_X . |
| 20° | 0.935 | 24.71 | 212.4 | 188 | 0.9585 | 25.11 | 210.4 | 195 |
| 30 | 0.926 | 23.90 | 212.4 | 188 | 0.9510 | 24.23 | 210.1 | 193 |
| 40 | 0.917 | 23.09 | 212.7 | 191 | 0.9397 | 23.53 | 211.1 | 196 |
| 50 | 0.907 | 22.27 | 213.2 | 194 | 0.9300 | 22.68 | 211.3 | 197 |

These values are lower than those required either for the simple ring structure (I) or the bridge-ring structure (VI) except that the methyl group is replaced by H. Nevertheless the mean of the values in Table II is nearer the value for the simple ring structure and is much away from the value for the bridge-ring.

In the case of dimethylpyrone (II), which was purified by double crystallisation and which was dissolved in nitrobenzene (as its solubility in ethyl acetate is small), the following results were obtained,

TABLE III.

Dimethylpyrone.

| Temp. | Density. | γ | P_K | P_X | Density. | γ | P_K | P_X |
|-------|------------------|----------|-------|-------|----------|------------------|-------|-------|
| | $\alpha = 0.164$ | | | | | $\alpha = 0.118$ | | |
| 50° | 1.166 | 39.48 | 265.0 | 304 | 1.164 | 37.34 | 261.4 | 309 |
| 60° | 1.154 | 36.79 | 262.2 | 299 | 1.154 | 36.69 | 262.9 | 316 |
| 70° | 1.143 | 36.04 | 264.2 | 311 | 1.148 | 34.77 | 260.5 | 300 |

Table III also brings out the difference between the observed values and those calculated for either for the simple ring structure (II) or the bridge-ring structure; the observed values being higher than the values required for the structures (VI). Nevertheless the observed values are nearer that corresponding to simple ring structure.

Observed results indicate that pyrone (I) and diethylpyrone (III) are simple ring compounds, while dimethylpyrone (II), which comes in between the two, is a bridge-ring compound. This is probable when taken in conjunction with the fact that at ordinary temperature (about 32°) both pyrone and diethylpyrone are liquids; but dimethylpyrone is a high melting solid, or there is possibly some other kind of complexity in the molecule of dimethylpyrone. But it is significant that where chemical means could not explain why a middle member is a high melting solid, while its two neighbours are liquids, it could be explained at least to some extent by "parachor".

Dehydracetic acid (VIII) which is a pyrone was also studied and the following results were obtained when dissolved in nitrobenzene.

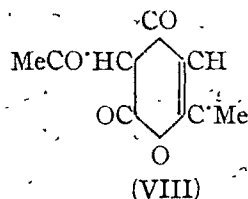


TABLE IV.

Dehydracetic acid.

| Temp. | Density. | γ | P_K | P_X |
|--|----------|----------|-------|-------|
| $P_{calc.} \text{ (VIII)} = 374.1, \alpha = 0.151$ | | | | |
| 40° | 1.204 | 40.98 | 272.7 | 372.3 |
| 50° | 1.196 | 38.9 | 272.4 | 370 |
| 60° | 1.186 | 38.19 | 272.3 | 369 |
| 70° | 1.177 | 36.91 | 272.0 | 368 |

The agreement between the value for the accepted formula (VIII) and the observed value is quite close.

Diacetylacetone, a 1:3,5-triketone, closely related to pyrones, was chosen for our study. Deshapande (*loc. cit.*) on chemical grounds gave it the formula (IV) but to which Collie has given the formula (VII). Table V shows the value of the parachor obtained for diacetylacetone dissolved in ethyl acetate.

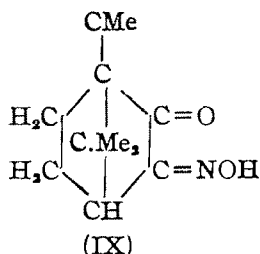
TABLE V.

Diacetylacetone.

| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ | P_M . | P_X . |
|-------|-------------|------------|---------|---------|----------|-------------|---------|---------|
| | $x=0.167$. | | | | | $x=0.183$. | | |
| 20 | 0.9473 | 24.91 | 229.0 | 298 | 0.9363 | 25.71 | 235.9 | 324.6 |
| 30 | 0.9399 | 24.10 | 229.2 | 300 | 0.9287 | 24.91 | 235.8 | 324 |
| 40 | 0.9290 | 23.29 | 229.5 | 302 | 0.9212 | 24.02 | 235.3 | 322 |
| 50 | 0.9213 | 22.41 | 229.5 | 302 | 0.9093 | 23.29 | 236.5 | 328 |
| 60 | 0.9120 | 21.50 | 229.5 | 302 | 0.9048 | 22.35 | 235.4 | 322 |

The value for structure (IV) is 334.2 and for the structure (VII) is 328. From these values alone it is difficult to decide in favour of either of the structures. The mean value observed from Table V is 324, which is fairly close to the value 328 corresponding to the bridge-ring structure. As diacetylacetone is derived from dimethyl-pyrone, it seems that the bridge-ring in the pyrone is retained when it changes to the corresponding triketone.

In the calculation of parachor for the bridge-ring such as shown in (VI) and (VII), a bridge-ring was assumed to be made of two rings each with five atoms. Whether such an assumption is justified must be tested by working with a substance in whose molecule the existence of a bridge-ring has been definitely proved. *iso*Nitrosocamphor (IX) having the same bridge-ring as in camphor was chosen for the purpose of experiment.



It could be purified by repeated crystallisations until the desired melting point is obtained. The following results were obtained with isonitrosocamphor dissolved in nitrobenzene.

TABLE VI.
isoNitrosocamphor.

$P_{\text{calc.}} = 438$.

| Temp. | Density. | γ . | P_M . | P_X . | Density. | γ . | P_M . | P_X . |
|-------|-------------------|------------|---------|---------|----------|--------------------|---------|---------|
| | $\alpha = 0.18$. | | | | | $\alpha = 0.198$. | | |
| 50° | 1.153 | 38.62 | 288.4 | 440 | 1.149 | 39.26 | 291.2 | 438 |
| 60 | 1.144 | 37.34 | 288.3 | 440 | 1.141 | 37.87 | 290.7 | 436 |
| 70 | 1.136 | 36.04 | 288.3 | 440 | 1.132 | 36.49 | 290.0 | 433 |
| 80 | | | | | 1.120 | 35.30 | 290.5 | 435 |

There is a close agreement between the values of parachor observed and found from the above tables and the value required for the formula (IX).

This proves that for the purpose of calculation of parachor of a substance containing a bridge-ring in its molecule, a bridge-ring may be taken to be equal to two simple rings.

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PROPERTIES OF DIALYSED HYDROUS ALUMINA HYDROSOLS

PART I. p_H CHANGES DUE TO AGEING AND TITRATION WITH NEUTRAL SALTS.

BY N. P. DATTA.

On ageing the p_H of hydrous alumina hydrosols slightly decreases and then becomes almost constant. Sols which contain free acids are more stable and give the same amount of chlorine on conductometric titration with different silver salts. Highly pure sols are less stable and the amount of chlorine obtained by conductometric titration with silver salts is in the order: sulphate < nitrate < acetate. The chlorine obtained by conductometric titration is less than the free or total chlorine content of the sols but in the case of less pure sols, this is almost equal to the free or the total chlorine content of them. Chlorine appears to be present in three different states. A part is free and the other bound. The former is made up of chlorine present in the intermicellary liquid and chlorine present in the mobile sheet of the double layer. As the purification of the sols by electrodialysis proceeds and the p_H rises, the portion of total chlorine associated with the colloidal particles, which remains 'bound' with the particles, increases. Neutral salts decrease the H^+ ion activity and increase the Cl^- ion activity of the sols. The order of effectiveness of the anions in both cases is chloride < sulphate < oxalate < ferrocyanide. A probable constitution of these sols has been suggested.

The electrochemical properties of colloidal hydrous alumina have been studied by several workers. Pauli and his co-workers (Adolf and Pauli, *Kolloid Z.*, 1921, **29**, 281; Pauli and Valko, *Z. physikal. Chem.*, 1926, **121**, 164; Pauli and Schmidt, *ibid.*, 1927, **129**, 199; Pauli and Muttone, *Kolloid Z.*, 1931, **57**, 312; "Elektro chemie der Kolloide", 1929, p. 545) concluded from titration experiments with silver salts that the whole of the chlorine was in the reactive stage and considered these sols to be dispersions of basic salts having the composition $[mAl(OH)_3.nAlOCl.AlO^+] Cl^-$. Thomas and his co-workers (Thomas and Whitehead, *J. Phys. Chem.*, 1931, **35**, 27; Thomas and Tai, *J. Amer. Chem. Soc.*, 1932, **54**, 841; Thomas and Von Wicklen, *ibid.*, 1934, **56**, 794; Whitehead and Clay, *ibid.*, 1934, **56**, 1934; Whitehead, *Chem. Reviews*, 1937, **21**, 113) considered that hydroxyl groups of highly basic salts of aluminium combine with one another to form 'ol' and ' μ ol' complexes. These complexes go on increasing till the aggregates formed by such linkages attain colloidal dimensions. According to them on the addition of an electrolyte its anions penetrate the complex and displace aquo or other anions present there. H^+ ions can also enter the complex and neutralise the hydroxo groups. The phenomena of ageing, the changes of p_H occurring on the addition of neutral salts etc. were interpreted on this basis. Weiser (*J. Phys. Chem.*, 1920, **24**, 505;

1931, **35**, 1368, "Inorganic Colloid Chemistry", 1935, **II**, pp. 104-118) has pointed out that there was no direct evidence of the existence of a basic chloride and the assumption that alumina sols were basic complexes was not supported by X-ray analysis. According to him the interaction of alumina sols with electrolytes occurs in the electrical double layer surrounding the particles. The inner layer is supposed to contain Al^{+++} and H^+ ions and the outer layers Cl^- ions, a part of the Cl^- ions is rendered immobile being held by electrostatic forces. On the addition of electrolytes its anions are adsorbed in the outer layer and this is followed by an increased adsorption of cations. Multivalent ions would reduce the thickness of the double layer and so cause coagulation. During coagulation both anions and cations tend to be desorbed due to the diminution of the specific surface. Mattson (*Soil Sci.*, 1930, **30**, 459) represented the composition of positively charged aluminium hydroxide as $(Al_2O_3)_x \cdot Al_2O_3^{++} + 2Cl^-$ and of negatively charged hydroxide as $Al(OH)_2OH^- + Na^+ \cdot Al^-$. Though it is generally assumed that NaOH forms the aluminate $NaAlO_2$, he considers that on the surface of the colloid and specially of soil colloids, a simple addition compound like the above is formed. Nikolsky and Parámonova (*Z. physikal. Chem.*, 1932, **159**, 47) from a potentiometric study of the precipitation of aluminium salts with NaOH concluded that aluminium hydroxide in the colloidal state consisted of micelles on the surface of which there were $Al(OH)_3$ molecules and $Al(OH)_2^+$ and AlO_2^- groups formed respectively by the basic and acidic dissociation of the amphoteric hydroxide. In the outer layer there were the corresponding OH^- and H^+ ions which could again be replaced by the cations and anions respectively of an added electrolyte. The basic dissociation would predominate below the isoelectric p_H and the acidic dissociation above it. The electrochemical properties of aluminium hydroxide sols have been studied previously in this laboratory (Mukherjee *et al.*, *J. Indian Chem. Soc.*, 1933, **10**, 405; *Indian J. Agric. Sci.*, 1934, **4**, 733; Mukherjee, *Kolloid Z.*, 1933, **63**, 36; 1933, **65**, 72). It has been observed that on dilution the p_H , specific conductivity and the chloride ion activity of the sol vary in a manner which is different from what would be expected of an electrolyte in true solution. Calculation of the specific conductivity, taking into account the amounts of electricity carried by the colloidal particles and by the oppositely charged ions, showed disagreement with the observed specific conductivities.

The sols used by these and other workers, however, had a fairly low p_H and high specific conductivity and probably contained free acids (or aluminium salts). The present investigation deals with a comparison of the properties of sols having different degrees of purity. Sols A and B have

low p_H and high specific conductivity and are similar to the sols used by other workers. Sols C, D, and E are of greater purity. Changes in p_H due to ageing and interaction with silver and potassium salts have been reported in this paper. The interaction of the sol with different electrolytes has been considered to occur in the electrical double layer surrounding the particles. The double layer has the following structure (*cf.* Mukherjee, *Trans. Faraday Soc.*, 1921, **16**, 103; *Phil. Mag.*, 1922, **44**, 321). Its inner layer probably consists of primarily adsorbed Al^{+++} , AlO^+ and AlO_2^- ions. The relative amounts of these ions and the ratio of positive to negative charges depend on the p_H of the system. Hydroxyl, chloride or other anions and H^+ ions are present in the double layer partly in secondarily adsorbed *i.e.* bound condition and partly in a mobile, osmotically free condition. The relative amounts in these conditions again depend on the p_H and the composition of the intermicellary liquid.

According to this view chlorine, present in the sol, is likely to occur in different states. Part of the total chlorine, Cl_T , is present in association with the colloid particles, *i.e.* the micellar chlorine, Cl_M . The remaining part, the intermicellary chlorine, Cl_{IM} , is present in the intermicellary liquid. Micellar chlorine, Cl_M can be further subdivided into two fractions: one is osmotically active, denoted by $(Cl_M)_r$, and the other, osmotically inactive, denoted by $(Cl_M)_b$.

Hence

$$Cl_T = Cl_M + Cl_{IM} = (Cl_M)_b + (Cl_M)_r + Cl_{IM}$$

and total free chloride,

$$Cl_f = (Cl_M)_r + Cl_{IM} = Cl_T - (Cl_M)_b.$$

EXPERIMENTAL.

Kahlbaum's pure $AlCl_3 \cdot 6H_2O$ was purified (Dennis, *Z. anorg. Chem.*, 1895, **9**, 339) and hydrous alumina gel was precipitated from its solution in equilibrium water (sp. conductivity = 1.15×10^{-6} mho at 35°) by Merck's liquor ammonia diluted with equal volume of water. The gel was peptised completely by washing in a centrifuge and the resulting sols purified by ordinary dialysis. Sol A was dialysed for three weeks and sol B for a period extending over $1\frac{1}{2}$ months. In the case of sols C, D and E, further purification has been effected by electrodialysis after dialysis lasting for 2 to 3 weeks. The hydrous alumina contained adsorbed ammonia which was not easily removed by washing in the centrifuge and was only slowly removed during dialysis. On prolonged electrodialysis most of the alumina was precipitated in flocks and dilute sols were obtained.

A Tinsley vernier potentiometer in conjunction with a Hartmann and Braun galvanometer (type 159) was used for measuring the E.M.F. The p_H was measured by the hydrogen electrode against normal calomel electrode* using saturated KCl in the bridge. The hydrogen gas was obtained by the electrolysis of caustic soda solution in a U-tube with platinum electrodes. The gas was purified by passing it through concentrated sulphuric acid, soda lime, a tube containing copper gauze heated in an electric furnace (400°) and finally through soda lime and conductivity water. The Cl^- ion activity was measured with Ag-AgCl electrode (Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532) in conjunction with another Ag-AgCl electrode placed in 0.1N-KCl solution using saturated NH_4NO_3 in the bridge. The potentiometric and conductometric titrations were carried out in pyrex glass titration cells provided with air-tight ground glass joints (*Indian J. Agric. Sci.*, 1936, **6**, 519) which allowed simultaneous measurement of chloride and hydrogen ion activities. The assembly for the measurement of specific conductivity consisted of an oscillator working at 500 and 1000 cycles per second, a non-inductive resistance box and a marble drum bridge. A condenser of variable capacity was connected in parallel with the resistance box in order to balance the capacity of the cell. The alumina content was estimated as Al_2O_3 . Total chlorine was estimated by potentiometric titration with silver salts after solution of the sol in nitric acid by Ag-AgCl electrodes. A water thermostat covered with a layer of oil has been used at $35 \pm 0.05^\circ$.

For sols having very low hydrogen and chloride ion activities and low specific conductivities, the measurement of the E.M.F. is attended with various difficulties. Electrical leakages often prove very troublesome; to obviate this the metal cover of the experimental table, the lead outer covers of the electrical connections and all exposed terminals etc. were earth connected. The temperature of the room was kept a little higher than the surroundings in order that moisture may not condense on the terminals. To eliminate diffusion of KCl from the beaker containing saturated KCl, into the cell, the U-tube connecting the latter with the beaker was fitted with a stop-cock. Before the measurements the U-tube was taken out and the piston of the stop-cock rinsed with KCl and replaced. The tube was then washed thoroughly with water, filled with the sol and inserted into its position in the cell with the stop-cock closed. The junction potential was eliminated as usual by interposing a saturated KCl bridge. It is well known, however, that complete elimination of the junction potential is not effected thereby. The results obtained in this laboratory with some

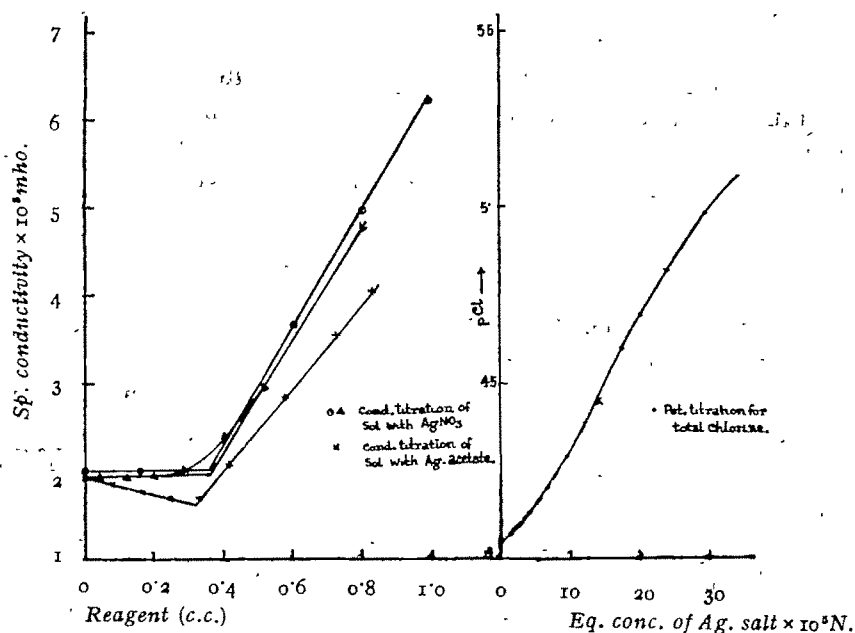
* The E.M.F. of N-calomel electrode was taken as 0.2823 volt at 35° (Sørensen and Linderstrøm Lang, *Compt. rend. Lab. Carlsberg*, 1924, 25)

solutions of HCl (Mitra, *Indian J. Agric. Sci.*, 1940, **10**, 318) illustrate the reliability of the technique and of the electrodes used in these measurements. Using this technique and following the method used by the author in the case of stearic acid sols (Mukherjee and Datta, *J. Indian Chem. Soc.*, 1939, **16**, 563), the reproducibility of the p_H measurements as carried out on different days was fairly satisfactory, the limits of reproducibility being 0.01 p_H unit (Table II).

In order to test the accuracy of Ag/AgCl electrode measurements, several Ag/AgCl electrodes were prepared. The chloride ion activities of HCl at two dilutions were measured with these electrodes and care was taken to make the system free from air. The E.M.F. of the concentration cell was reproducible within 0.1 millivolt. The following data show the agreement between the observed and the calculated E.M.F.

Cell : $\text{Ag}/\text{AgCl}/0.001N\text{-KCl}/\text{saturated NH}_4\text{NO}_3/0.01N\text{-KCl}/\text{Ag}/\text{AgCl}$
 Observed E.M.F. = 0.0610 volt at 35°.

FIG. 1.



The E.M.F. calculated from the activity coefficients given by Randall and Young ("Thermodynamics", 1923) is 0.0594 volt at 25°. The E.M.F. of the electrodes was also sufficiently reproducible. The titrations were

repeated in some cases to check the reproducibility. The agreement among the duplicated curves was fairly satisfactory (Fig. 1).

Composition of Sols.

TABLE I.

| Sol | Alumina content in g. moles per litre. | Al ⁺⁺⁺ ion | Free Cl ⁻ ion (Cl _r) in g. moles per litre. | Total Cl (Cl _r) in g. moles per litre. | NH ₃ . | p _H | Sp. condy (mho). |
|-----|--|-----------------------|--|--|-------------------|----------------|-------------------------|
| A | 1.37 × 10 ⁻³ | Nil | 13.18 × 10 ⁻⁵ | 13.75 × 10 ⁻⁵ | Nil | 4.73 | 19.3 × 10 ⁻⁶ |
| B | 0.78 | , | 7.65 | 9.78 | , | 5.60 | 15.60 |
| C | 1.25 | , | 6.30 | 8.10 | , | 6.42 | 8.80 |
| D | 1.30 | , | 3.40 | 8.00 | , | 6.51 | 7.06 |
| E | 0.62 | , | 2.25 | 6.04 | , | 6.70 | 5.20 |

None of these sols contains either any free aluminium ions or ammonia as shown by ultrafiltrate test of the sol with 8-oxyquinoline or Nessler's reagent. With the progress of purification, the specific conductivity and the hydrogen and chloride ion activities of the sol appreciably decrease. The p_H of the sols C, D and E is nearly neutral and the specific conductivity is of the order of the equilibrium water used. Sols A and B, however, are less pure than the other two. From columns 4 and 5 (Table I) it is apparent that the whole of the chlorine is not osmotically active (free).

p_H Changes due to Ageing.

Hydrous alumina hydrosols have been observed to undergo with time changes in p_H. Thomas and Whitehead (*loc. cit.*) found an increase in p_H of aluminium oxychloride hydrosols due to ageing at 20°. In 54 days the p_H increased from 4.54 to 4.75 and from 4.56 to 5.4 for two different sols. Thomas and Tai (*J. Amer. Chem. Soc.*, 1932, **54**, 841) working with aluminium oxyiodide sols at 90° obtained a decrease in p_H after ten days but on further ageing the p_H increased. But Weiser (*loc. cit.*) using three sols observed uniformly a decrease of 0.39 to 0.13 p_H units in about 3 months. Pugh (*Soil Sci.*, 1934, **37**, 403) prepared a sol from isoelectric precipitates and observed that the p_H changed from 7.31 to 4.57 in 40 days and the p_H did not remain constant thereafter. On the other hand, B. Majumdar (*unpublished work*) in this laboratory found that neglecting some erratic variations the p_H remained almost constant after some time.

TABLE II.
 p_H Changes on ageing.

| Sol A | | Sol C. | | Sol D. | |
|---------|---------|----------|---------|----------|---------|
| Date. | p_H . | Date. | p_H . | Date. | p_H . |
| 4-8-38 | 5'26 | 12-11-38 | 6'93 | 19-9-39 | 7'08 |
| 6-8-38 | 5'06 | 13-11-38 | 6'90 | 28-9-39 | 7'02 |
| 10-8-38 | 4'95 | 26-11-38 | 6'88 | 5-10-39 | 7'00 |
| 11-8-38 | 4'82 | 23-12-38 | 6'42 | 20-11-39 | 6'62 |
| 9-2-39 | 4'75 | 27-12-38 | 6'42 | 29-11-39 | 6'51 |
| 22-4-39 | 4'75 | 4-1-39 | 6'42 | 2-12-39 | 6'51 |
| | | 15-1-39 | 6'43 | 7-12-39 | 6'51 |

FIG. 2.

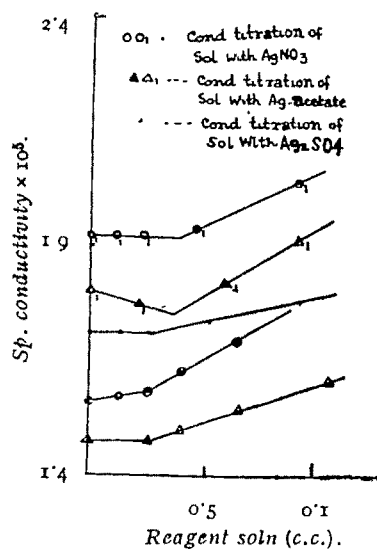
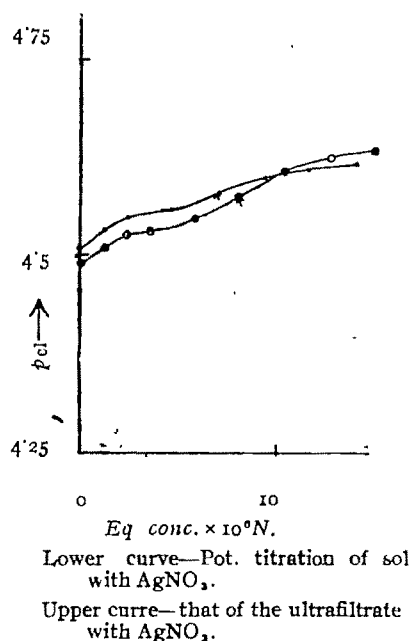


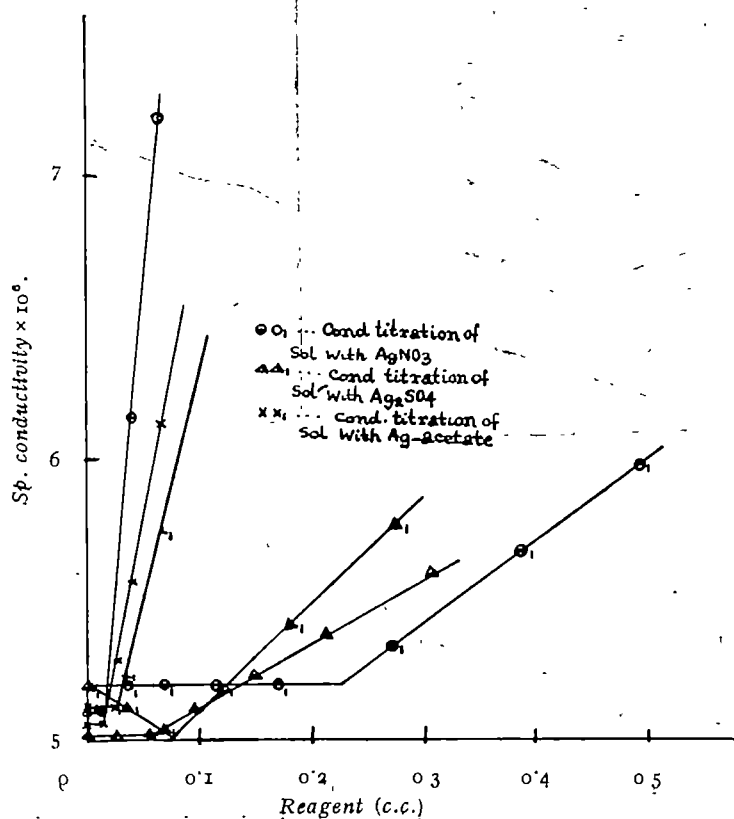
FIG. 3.



It will be found that the p_H of all these sols decreased gradually and ultimately reached practically constant values. While it is simpler to ascribe this decrease in p_H to the slow hydrolysis of the adsorbed aluminium salts present on the surface of the particles, Thomas and Whitehead (*loc. cit.*) explained the increase observed by them in terms of their colation and oxolation theories according to which H^+ ions from the solution enter the sol

complex and neutralise the hydroxo groups. Aluminium hydroxide sols probably contain hydroxo groups in their micelles (discussed later) but whether H^+ ions do or do not enter the complex colloidal micelle during ageing in the manner suggested is an open question. An examination of the data in Table I of their paper shows that sols probably contained ammonia which was slowly desorbed and neutralised by hydrogen ions and the p_H increased in consequence. Their sol B containing the largest amount of ammonia showed the largest p_H increase. Weiser (*loc. cit.*) ascribed the decrease in p_H observed by him to the liberation of stabilising hydrogen ions from the colloidal micelles due to coalescence with age but the slow hydrolysis of adsorbed aluminium chloride, which was used by him for peptisation, is a contributory factor. The surprisingly large decrease in p_H observed by Pugh (*loc. cit.*) is very probably the result of the hydrolysis of large amounts of aluminium chloride likely to be present under the conditions of preparation of the sol.

FIG. 4.
Hydrous alumina sol E—Ag salt titration.



PROPERTIES OF DIALYSED HYDROUS ALUMINA HYDROSOLS

Titration with Silver Salts.

Pauli and Schmidt (*loc. cit.*) and later Thomas and Tai (*loc. cit.*) found that conductometric titration of aluminium hydroxide sols with different silver salts gives a constant amount of chlorine which is identical with the total amount obtained by dissolving the colloid in nitric acid. Raychaudhury, Sen and Chatterjee (*J. Indian Chem. Soc.*, 1934, **11**, 13) obtained a greater value on titration with silver acetate than silver nitrate.

Sols A, B, C, D and E have been titrated conductometrically and the sol D, both conductometrically and potentiometrically, with silver acetate, nitrate and sulphate. Total chlorine in the sols has been determined by potentiometric titration. The titration curves for sols A, B, D and E only are shown in Figs. 1-4. The amounts of chlorine obtained from the inflexion points of these curves and also from those not shown are given in Table III.

TABLE III.

| Reagent | | | Reagent | | |
|-------------------------------------|----------|---|---|-----------|---|
| Vol. reqd at the break. | Strength | Amount of chlorine* (g. moles per litre). | Vol. reqd. at the break. | Strength | Amount of chlorine* (g. moles per litre). |
| Sol A (30 c.c.) | | | Sol D (25 c.c.) | | |
| 0.36 c.c. of AgNO ₃ | 0.011 N | 13.04 × 10 ⁻⁶ | 0.205 c.c. of AgNO ₃ | 0.00098 N | 0.79 |
| " " | " | 13.04 | 0.180 c.c. of Ag ₂ SO ₄ | 0.00097 N | 0.69 |
| 0.315 c.c. of Ag-acetate | 0.0126 N | 13.09 | | | 0.80 † |
| | | 13.75** | | | 0.69 † |
| Sol B (50 c.c.) | | | | | 8.0** |
| 0.038 c.c. of AgNO ₃ | 0.0066 N | 0.50 | Sol E (50 c.c.) | | |
| 0.026 " " | 0.01 N | 0.51 | 0.014 c.c. of AgNO ₃ | 0.01 N | 0.28 |
| " " Ag ₂ SO ₄ | 0.01 N | 0.51 | 0.225 " " " | 0.00066 N | 0.29 |
| 0.039 " Ag acetate | 0.0065 N | 0.51 | 0.075 " " Ag ₂ SO ₄ | 0.00066 N | 0.10 |
| 0.026 " " | 0.0098 N | 0.51 | 0.0525 " " " | 0.001 N | 0.1 |
| | | 9.78** | 0.016 " " Ag acetate | 0.0098 N | 0.31 |
| Sol C (30 c.c.) | | | | | |
| 0.09 c.c. of AgNO ₃ | 0.0011 N | 0.32 | 0.026 " " " " | 0.0065 N | 0.33 |
| 0.03 c.c. of Ag-acetate | 0.0034 N | 0.33 | | | 6.04** |
| | | 8.2** | | | |

* Estimated by conductometric titration except where stated otherwise.

** Total chlorine by pot. titration with AgNO₃.

† Chlorine by pot. titration of ultrafiltrate with AgNO₃.

‡ Do. by " " of sol " "

Conductometric titration of sol A with the acetate and the nitrate gives an amount of chlorine, Cl_0 which is very nearly equal to the free chlorine, Cl_F , calculated from the E.M.F. of the Ag-AgCl electrode but is somewhat smaller than Cl_T obtained by analysis. In the case of sols B, C, D and E, however, Cl_0 is much smaller than Cl_T and even Cl_F . Cl_0 is definitely greater than the chlorine found in the ultrafiltrate of the sol (*cf.* Sol D, Fig. 5). Titration with different silver salts gives values in the order: sulphate < nitrate < acetate. The percentages of $(\text{Cl}_M)_B$, $(\text{Cl}_M)_F$, Cl_M in terms of Cl_T are given in Table IV.

TABLE IV.

| Sol. | Cl_T expressed in g | Cl_F moles. per litre. | Cl_M | Cl_M expressed in | $(\text{Cl}_M)_F$ in | $(\text{Cl}_M)_B$ % Cl_T . |
|------|---------------------------------|------------------------------------|-----------------------|-------------------------------|-------------------------|--|
| A | 13.75×10^{-5} | 13.18×10^{-5} | ... | .. | ... | 4.1 |
| B | 9.78 | 7.65 | .. | ... | ... | 20.0 |
| C | 8.2 | 6.3 | ... | ... | ... | 23.1 |
| D | 8.0 | 3.2 | 0.69×10^{-5} | 92.0 | 21.5 | 60.0 |
| E | 6.04 | 2.25 | ... | ... | ... | 62.7 |

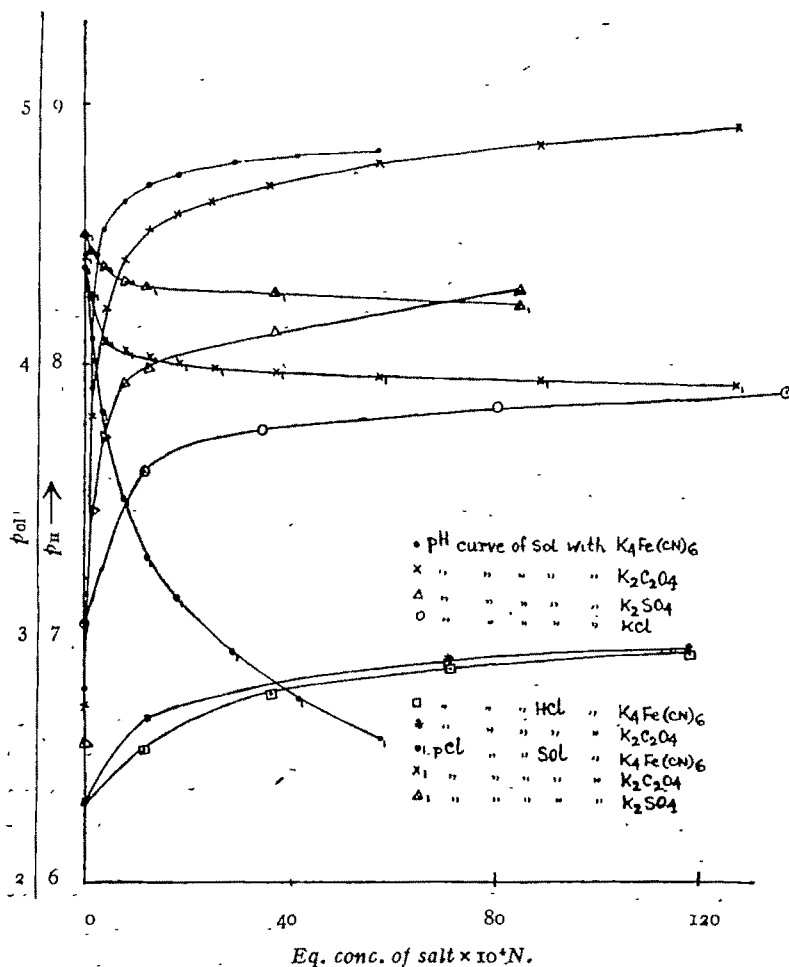
The amount of the osmotically inactive chlorine $(\text{Cl}_M)_B$ in the different sols is in the order: sol E > sol D > sol C > sol B > sol A. The H^+ ion concentrations and specific conductivities of the sols are in the reverse order.

Titration with Neutral Solution of Potassium Salts

Thomas and Whitehead (*loc. cit.*) and Thomas and Tai (*loc. cit.*) observed an increase of the p_H of hydrous alumina sols on titration with potassium salts; with the oxalate or acetate the p_H passed through a maximum. They attributed the rise in p_H to the replacement of hydroxo groups of the complex by anions, and considered that the oxalate was more effective because of its greater 'penetrating power'. The subsequent decrease was explained as arising out of "salt effects." The simultaneous displacement of chloride ions by the salt solutions has not been recorded in the above paper. Weiser (*loc. cit.*) found that Cl^- ions were displaced. The rise in the p_H of the sol obtained on the addition of potassium oxalate was attributed to the slight alkalinity of the $\text{K}_2\text{C}_2\text{O}_4$ solutions.

Changes in the hydrogen and chloride ion activities of sol D consequent on the addition of neutral* normal solutions of KCl, K_2SO_4 , $K_2C_2O_4$ and $K_4Fe(CN)_6$ have been shown in Fig. 5. The neutral salts decrease the

FIG. 5.



activity of hydrogen ions and increase that of the chloride ions to a marked degree. The change is at first rapid, then more slow and ultimately almost constant values are reached. The order of effectiveness of anion in raising the p_H and in decreasing the p_H is the same, namely chloride

* The p_H of the salt solutions was adjusted to 7.0, on adding small amounts of acid or alkali. This did not materially alter the concentration of the anion in the solution.

< sulphate < oxalate < ferrocyanide. The final p_H in all cases is on the alkaline side and for the oxalate and the ferrocyanide it rises to about 8.75. A comparison with the rise in p_H on adding these salts to water containing a trace of HCl to bring the p_H near about that of the sol (Fig. 5) shows that the increment in p_H is not due to the alkalinity of the salt solution as suggested by Weiser (*loc. cit.*) but should be ascribed to the displacement of OH^- ions by the anions.

In the titration with ferrocyanide, the Ag/AgCl electrode appears to have been poisoned as the displaced chlorine is greater than the total concentration of chlorine in the sol.

Structure of the Micelles.

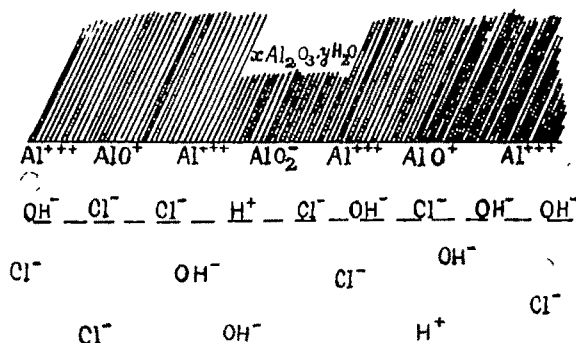
The views of Pauli and Valko (*loc. cit.*), Thomas and Whitehead (*loc. cit.*) and of Weiser (*loc. cit.*) regarding the micellar structure of hydrous alumina sols have been fully described by Weiser ("Inorganic Colloid Chemistry", Vol. II, 1935). The results described above admit of a simple explanation if the following structure is ascribed for the micelles :

The core of the micelle has the composition xAl_2O_3, yH_2O . The isoelectric p_H is 8.2 for alumina precipitated from the chloride (Mattson, *Soil Sci.*, 1930, **30**, 459). In the titrations of aluminium salts with alkalis, precipitation of alumina begins at about p_H 3.5 and is complete at p_H about 6.8. Above this p_H the precipitated alumina dissolves in the alkali and solution is complete at about p_H 10.9 with the formation of $NaAlO_2$ (Further discussed in Part II of this series ; also Britton, *J. Chem. Soc.*, 1925, **127**, 2120; Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 864; Blum, *ibid.*, 1913, **35**, 1499). The dissociation constant of aluminic acid $HAIO_2$ can be taken to be of the order of 10^{-10} *. It is reasonable to assume that during the precipitation of hydrous alumina by alkalis from aluminium salts, in the acid region the solution will contain Al^{+++} , H^+ and probably AlO^+ ions. The latter is probably formed near about p_H 6 and occurs for the case in which chloride ions are adsorbed on the surface near this region perhaps to form $AlOCl$ (*Indian J. Agric. Sci.*, 1934, **4**, 733). In the alkaline region, on the other hand, the system will contain OH^- and AlO_2^- ions. In the intermediate range of p_H , all these positive and negative ions will be simultaneously present, their relative proportion being determined by the

* Regarding the dissociation constant of aluminic acid there is some controversy (cf Blum, *loc. cit.*; Mahin, Ingraham and Stewart, *J. Amer. Chem. Soc.*, 1913, **35**, 30; Slade, *Z. anorg. Chem.*, 1912, **77**, 457)

prevailing p_H . Hydrous alumina during precipitation therefore will contain on its surface a primarily adsorbed layer of ions (Mukherjee, *loc. cit.*) both positive and negative ions, their relative numbers depending on the p_H of the sol. If this p_H is low, the ratio of primarily adsorbed positive to negative ions will be large or practically infinite and the particles will be positively charged. On the other hand, if the p_H is high, this ratio will be small or practically zero and the particles will be negatively charged. The positive ions on the surface, Al^{+++} or AlO^+ , will draw an equivalent number of negatively charged ions, OH^- , Cl^- , near them, some of which will be secondarily adsorbed neutralising a portion of the positive charge. The rest of the balancing negatively charged ions balancing the free positive charge will be in the diffuse or mobile sheet of the double layer. A similar relation holds for the negatively charged ions AlO_2^- on the surface, the balancing ions in this case being cations *e.g.*, H^+ ions and the cations of the added base. The proposed structure is diagrammatically represented in Fig. 6.

FIG. 6.



[The ratio of +ve to -ve primarily adsorbed ions depends on p_H].

DISCUSSION.

Titration with Silver Salts.—The silver salts first react with the free chloride in the intermicellary liquid and then with the mobile and bound chloride ions of the double layer. The chlorine of the primarily adsorbed layer and that present as $AlOCl$ will be the last to react. The extent to which the reaction will proceed appears to be conditioned by the stability of the sol. The silver salts tend to coagulate the sol. If the sol is not sufficiently stable, coagulation may set in before the chlorine has completely

reacted with the silver salt and a considerable part may be blocked within the coagulum and thus left unreacted upon. This accounts for the much smaller Cl_o than Cl_r or Cl_f of sols B, C, D and E. For sol A, Cl_o is equal to Cl_r and very nearly equal to Cl_f . This sol unlike others has a definitely acid reaction and the p_H is low enough to ensure the presence of Al^{+++} and AlO^+ ions on the surface as a primarily adsorbed layer. That coagulation plays a part in the estimation of the chlorine by conductometric titrations is indicated by the fact that the Cl_o values obtained with different silver salts are in the order $SO''_4 < NO'_3 < Ac'$. The relative effects of these anions on the coagulation of positively charged hydrous alumina sols are also in this order.

In the titration with salts or acids, the p_H of the sols is in the alkaline and acidic regions respectively and hydrous alumina sols are known to be stable in acidic or alkaline regions, whereas in the titration with silver salts, the p_H remains near about the neutral region where it is the least stable. It can therefore be understood why in the titration with silver salts the sols get coagulated more quickly and chlorine obtained is less and follows the order that is found. It is also possible that in the initial stages sulphate displaces more chlorine and more $AgCl$ is formed than either with the nitrate or acetate. The $AgCl$ may thus form a greater coating on the colloid particles and thus the particles escape reaction and a smaller amount of chlorine reacts with the sulphate.

Pauli and Schmidt (*loc. cit.*) have interpreted their results to mean that the whole of the chlorine is in the reactive state. But it appears from the low p_H value (4.51) of their sols, that they were similar to, but more stable than sol A. It does not appear difficult therefore to see why these authors obtained the same total amount of chlorine by conductometric titration with different silver salts.

Titration with Potassium Salts:—The change in p_H and p_{cl} with the addition of K salts is significant. It shows simultaneous presence of OH^- and Cl^- ions in the double layer and they are both displaced by the anions of the salt solutions. The observed changes can be explained as follows:

On the addition of a salt, its anions enter into the diffuse or mobile layer of ions and are adsorbed secondarily to an extent depending on the condition. As a result of their penetration into the double layer, they displace OH^- and Cl^- ions into solution. The K^+ ions are not likely to be secondarily adsorbed to any large extent but they should be capable of displacing H^+ ions into solution. Two opposite forces have to be thus

taken into consideration so far as the p_H changes are concerned. These are the adsorption of anions which tend to increase the p_H and the adsorption of K^+ ions which tend to lower the p_H . Their relative magnitude depends again on the condition in the double layer. The amount of displacement of the different ions at any instant will depend on the ratio of positive to negative ions in the double layer at that instant. This ratio as has already been stated, depends on the p_H of the system. In the pure sol there is a preponderance of positive charges over negative charges. In the initial stages of the titration, the relative effect of the anions will therefore be greater than that of K^+ ions. The net effect will result in an increase in p_H . As the p_H increases, the ratio of positive to negative charges in the primarily adsorbed layer of ions decreases and the adsorption of K^+ ions and consequently the displacement of H^+ ions increases. In the later stages of the titration, the two opposing forces will balance and the p_H will remain constant. The anions of the added salt displacing Cl^- ions from the double layer into the intermicellary liquid increases the chloride ion activity of the sol.

C O N C L U S I O N.

Highly purified hydrous alumina hydrosols of high p_H and low specific conductivity (sols C, D and E) have been prepared by peptisation of hydrous alumina precipitated from purified aluminium chloride and pure ammonia and purified by dialysis and electrodialysis. Their electrochemical properties have been studied and compared with sols of lower p_H and higher specific conductivity prepared by the same method but purified only by ordinary dialysis (sols A and B).

On ageing, the p_H of hydrous alumina sols slightly decreases and then becomes almost constant.

In sols A and B same amount of chlorine is obtained by conductometric titration with different silver salts and this for sol A is almost equal to the total chlorine concentration of the sol. Conductometric and potentiometric titrations of sols C, D and E, however with different silver salts give an amount of chlorine which is much smaller than either the free or the total chlorine content of them. Further interesting is the observation that in conductometric titrations, sulphate gives a smaller amount of chlorine than nitrate and nitrate smaller than acetate.

The difference between the total chlorine and that contained in the ultrafiltrate represents the amount of chlorine that is present in association with the colloid particles of which part is free and part is bound.

As the sols become more and more pure, the percentage of bound chlorine becomes greater. Neutral salts decrease the H^+ ion activity and increase the Cl^- ion activity of the sols. The order of effectiveness of the anions in both cases is chloride < sulphate < oxalate < ferrocyanide.

A probable constitution of these sols has been suggested.

Thanks of the author are due to Prof. J. N. Mukherjee, for his suggestions and also for his kind and encouraging interest in the work and to the Calcutta University for the award of a Research Scholarship during the tenure of which this work was done.

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STUDY OF THE FATTY OIL FROM THE SEEDS OF STAR-ANISE.

BY J. W. ATRAN AND S. V. SHAH.

The fatty oil contains the following percentages of acids: myristic, 4.43, stearic, 7.93, oleic, 63.24, linolic, 24.4. The yield of the oil is 55% on the weight of the decorticated seeds.

Star-anise (N. O. Magnoliaceae) comprises several ever-green aromatic shrubs with coriaceous leaves, readily known by the arrangement of the one-sided carpels in one radiating whorl. When ripe, they are woody and split at the upturned ventral suture so that the seeds become visible. The carpels are used as an ingredient in curry powder, but the seeds are usually thrown away.

The present study deals with the fatty oil obtained from the seeds of the variety, obtained locally from the bazaar, and known as "badamful," and identified as *I. verum*. It is imported from China. A preliminary note on the subject appeared previously (*Current Sci.*, 1939, 8, 388).

It should be noted that Bulir (*Z. Nahr. Genussem*, 1912, 24, 309) has also studied the oils from two varieties of *Illicium*. His results are summarised below along with our results.

TABLE I.

| | <i>I. verum</i> (Bulir). | <i>I. religiosum</i> (Bulir). | Badamful (<i>I. verum</i>). Authors. |
|---------------|-----------------------------|----------------------------------|---|
| Yield | 20% | 12.5% | 55% |
| Iodine value | 93.1 | 90.6 | 88.36 |
| Sap. value | 193.8 | 193.4 | 194.5 |
| Liquid acids | 68.9% | 70.0% | 87.64% |
| Solid acids | 25.8% | 25% | 12.36% |
| Oleic acid | 45.0% | 60.2% | 63.24% |
| Linolic acid | 23.9% | 9.8% | 24.4% |
| Palmitic acid | 23.2% | 22.5% | — |
| Stearic acid | 2.6% | 2.5% | 7.93% |
| Myristic acid | — | — | 4.43% |

From the above table it appears that the oils Bulir has studied were quite different from each other as well as from the one we have studied. One of the oils obtained by Bulir had a fluorescence and both of them were yellow in colour. Our oil was reddish yellow in colour and had no fluorescence. Further, the figures for total solid fatty acids obtained by Bulir from the two oils are almost double of what we found in our oil. Even the composition is quite different. He finds no myristic acid in his oils whereas we find no palmitic acid in our oil.

EXPERIMENTAL.

The seeds were first decorticated, crushed and then extracted with petroleum ether in a Soxhlet apparatus, the ether from the extracted oil being removed by distillation, and the last traces by distillation under vacuum.

The oil has no particular taste. Its appearance is reddish yellow. Its physical and chemical constants are given in Table II.

TABLE II.

| | | | |
|---|--------|------------------------|--------|
| Yield (on the weight of decorticated seeds) | 55% | Sp. gr. at 25° | 0.9128 |
| Sap value | 194.5 | Acetyl number.. | 8.37 |
| Ref Index at 25° | 1.4677 | Reichert-Meissel value | 0.75 |
| Iodine value | 88.36 | Polenske number | 0.29 |
| Acid number | 11.65 | Unsaponifiable matter | 0.59% |

The Insoluble Fatty Acids.

The oil was saponified with alcoholic potash and then the alcohol was completely distilled off. The soaps obtained were dissolved in large quantities of water and the free fatty acids liberated by the addition of hydrochloric acid. The fatty acids (95%) which floated on the top were washed with water, filtered through a hot water funnel, and dried over calcium chloride. Their constants are given in Table III.

TABLE III.

Mixed Fatty Acids.

| | | | |
|--------------|-------|-------------|-------|
| Yield | 95% | Titre value | 20°C |
| Iodine value | 99.45 | Acid number | 203.5 |
| Mean M. W. | | 280.6 | |

Separation of Solid and Liquid Fatty Acids.

The mixed fatty acids were separated into solid and liquid acids by Twitchell's lead salt method (*Ind. Eng. Chem.*, 1921, 13, 806) when their percentages were found to be as follows :

| | |
|-------------------------|-------------------|
| Total mixed acids taken | 199.92 g. |
| Solid acids obtained | 23.8 g. (12.36%) |
| Liquid acids obtained | 168.7 g. (87.64%) |

The Solid Acids.

The lead salts were decomposed with dilute nitric acid, and the liberated fatty acids were taken up with ether. The ether extract was washed several times with water till the washings were no longer acid to methyl orange. On evaporating the ether, the solid acids were obtained, constants of which are given below.

TABLE IV.

| | | | |
|--------------|-------|-------------|-------|
| Percentage | 12.36 | Acid number | 215.5 |
| Iodine value | 2 | Mean M. W. | 259.9 |

Methyl Esters of the Solid Acids.

The solid acids were refluxed for nearly 4 hours with methyl alcohol, saturated with dry hydrogen chloride. The mixture was then poured into water and ether added. The ether extract was washed with a solution of sodium carbonate to remove any unesterified acids, and then after the evaporation of the ether, the esters were dried over anhydrous magnesium sulphate and then fractionally distilled under reduced pressure. The details are given in Table V.

TABLE V.

19 G. esters distilled under 2 mm. pressure.

| Fraction. | Temp. | Wt. | Sap. value. | Fraction. | Temp. | Wt. | Sap. value. |
|-----------|------------|---------|-------------|-----------|-----------|---------|-------------|
| I | Below 170° | 7.89 g. | 212.9 | IV | 180°-185° | 1.04 g. | 191.7 |
| II | 170°-175° | 3.3 | 208 | V | 185°-200° | 1.82 | 191.7 |
| III | 175°-180° | 1.82 | 198.5 | VI | Residue | 2.68 | 190.7 |

In the case of each of these fractions, acids were separated by fractional precipitation, and only myristic and stearic acids were isolated. Each fraction was hydrolysed and the acids obtained were dissolved in dilute acetone, when in each case the acid that crystallised out first, melted at 67-68° and had 281-283 as its molecular weight. The mixed melting point with each other in the case of these samples remained unchanged. Similarly the mixed melting point with an authentic sample of stearic acid remained unchanged. The mother-liquor in the case of each of the fractions yielded an acid melting at 52-53°, the melting point in each case with an authentic sample of myristic acid remaining unchanged. Molecular weight in all these cases was 228. The intermediate fractions were further fractionally crystallised when only these two acids were obtained.

In Table VI are given the calculated proportions, on percentage basis, of these two acids, fraction-wise. Corresponding theoretical saponification values of their methyl esters and mean molecular weights are also given, which compare well with observed values.

TABLE VI.

| Frac- tion. | % acids. | | S. V of methyl esters. | Mean M.W. | Frac- tion. | % Acids. | | S. V of methyl esters. | Mean M W. |
|----------------|-----------|----------|------------------------------|--------------|----------------|-----------|---------|------------------------------|--------------|
| | Myristic. | Stearic. | | | | Myristic. | Stearic | | |
| I | 50 | 50 | 209.7 | 256 | IV | 15 | 85 | 194.68 | 275.6 |
| II | 40 | 60 | 203.54 | 261.6 | V | 15 | 85 | 194.68 | 275.6 |
| III | 38 | 62 | 200.45 | 263 | Residue | 10 | 90 | 192.5 | 278.5 |

Total mean molecular weight calculated here, which is 263, compares well with the one actually observed (259.9). Thus the solid acids are, myristic, 35.8% and stearic, 64.2%.

Bromination of Liquid Acids.

The liquid acids (20 g.) were dissolved in 50 c.c. of glacial acetic acid. Separately bromine was mixed with equal volume of acetic acid, and the two were left in an ice-box for a while. Then the bromine solution was slowly added to the acids with constant shaking, till the colour of bromine persisted. The flask was kept in ice all along.

The flask was then kept in an ice-box overnight, and no solid was obtained. The whole was then poured into cold water and shaken with sodium thiosulphate to remove excess of free bromine. Then after the

removal of water, petroleum ether was added, and the whole mass stirred for a long time. Gradually a solid began to separate. The precipitate was transferred to a weighed filter paper and washed with cold petroleum ether till the filtrate became colourless. The solid bromo derivative was weighed and crystallised from alcohol, m.p. $113-14^{\circ}$; the bromine was estimated to be 52.84%. The weight of the bromide was 12.5 g. Ether was removed from the filtrate and again after washing with sodium thiosulphate, it was thoroughly dried. It weighed 22.62 g., and its bromine contents were 35.55%.

TABLE VII.

Acids taken for bromination = 20 g.

Oleic dibromide obtained = 22.62 g. (Found : Br, 35.55%. Calc. Br., 36.18%).

Linolic tetrabromide obtained = 12.5 g (Found : Br, 52.84%. Calc. Br, 53.33%).

Hence

12.5 G. of linolic tetrabromide = 5.566 g linolic acid. 22.62 G. of oleic dibromide = 14.43 g. of oleic acid.

Oleic acid present = 72.15%.

Linolic acid present = 27.83%.

This percentage composition of the liquid acids corresponds well to the iodine value of the mixed liquid acids, and that of the mixed solid and liquid acids already obtained.

Calculated mean iodine value for mixed liquid acids = 115.45

The one actually obtained = 114.5

The I. V. (calc. on the basis of 12.36% solid and 87.64% liquid acids) = 101.2

The one actually obtained = 99.45

Hence the percentage of the fatty acid contents of the oil works out as follows : Myristic acid, 4.43 ; oleic acid, 63.24 ; stearic acid, 7.93 ; linolic acid 24.4. Mean molecular weight calculated according to these figures comes to 279.3 which corresponds well to the observed value, 280.6.

CONDENSATION OF CHLORAL WITH 2-METHYL-4-QUINAZOLONE, 2-METHYL-3-AMINO-4-QUINAZOLONE AND SOME OF THEIR DERIVATIVES.

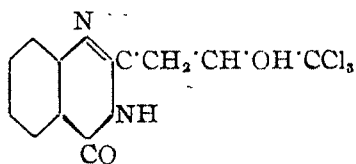
BY P. Y. KULKARNI.

Chloral condenses with 2-methyl-4-quinazolone and 2-methyl-3-amino-4-quinazolone giving rise in the former case to 2- γ -trichloro- β hydroxypropyl-4-quinazolone. The hydroxy group appears to be very labile as it is eliminated as a molecule of water on further reactions. The γ -trichloromethyl group hydrolyses on treatment with alkali giving an acrylic acid derivative. 2-Methyl-3- β -trichloro- α -hydroxyethylamino-4-quinazolone eliminates water on treatment with acetyl chloride.

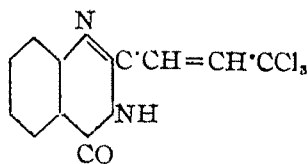
It is well known that a methyl group on a carbon atom, adjacent to the nitrogen atom of a basic heterocycle, as for instance in 2-methylpyridine, 2-methylquinoline, 4-methylquinoline and 2:4-dimethylquinoline etc. condenses with aliphatic aldehydes to form compounds of the type $R\cdot CH_2\cdot CH\cdot OH\cdot R$ and with aromatic aldehydes to form compounds of the type $ROH_2=CH\cdot R$.

An aliphatic aldehyde, such as chloral, has been condensed with 2-methylpyridine (Einhorn, *Annalen*, 1891, **265**, 208), 2-methylquinoline (Miller and Spaddy, *Ber.*, 1855, **18**, 3403), 4-methylquinoline (Königs and Muller, *Ber.* 1904, **37**, 1337), and 2:4-dimethylquinoline (Königs and Mengel, *Ber.* 1904, **37**, 1322), with a view to studying the products obtained by the alkaline hydrolysis of the γ -trichloromethyl group in the resulting compounds.

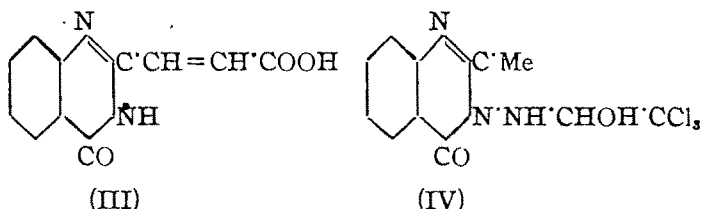
2-Methyl-4-quinazolone has been already condensed with aromatic aldehydes giving styryl compounds (Bogert and Beal, *J. Amer. Chem. Soc.*, 1910, **32**, 1654; 1912 **34**, 516). On the other hand chloral forms with it the intermediate aldol type of condensation viz., 2- γ -trichloro- β -hydroxypropyl-4-quinazolone (I).



(I)



(II)



The β -hydroxy group in 2- γ -trichloro- β -hydroxypropyl-4-quinazalone (I) readily eliminates as water, as on acetylation instead of giving the expected β -acetyl derivative it gives the $\alpha\beta$ -unsaturated compound (II). Similar tendency towards formation of $\alpha\beta$ -unsaturation was observed by Einhorn (*loc. cit.*) while preparing the β -chloro derivative of 2- γ -trichloro- β -hydroxypropylpyridine.

On treatment with concentrated caustic alkali the γ -trichloromethyl group in (I) hydrolyses to a carboxyl group with simultaneous elimination of a molecule of water and 4-quinazalone-2-acrylic acid (III) is obtained. Einhorn (*loc. cit.*), Miller and Spaddy (*loc. cit.*) and Königs and Mengel (*loc. cit.*) similarly obtained acrylic acid derivatives of pyridine, quinoline and 4-methylquinoline respectively, which on further oxidation gave the corresponding aldehydes.

It has been found that a primary aromatic amino group vigorously condenses with chloral with the formation of the compounds of the type $\text{R}'\text{N}=\text{CH}\cdot\text{CCl}_3$, and $(\text{RNH})_2:\text{CHCCl}_3$ according to the molecular proportion taken and no intermediate hydroxy compound could be isolated (Wheeler and co-workers, *J. Amer. Chem. Soc.*, 1908, **30**, 136). But 3-amino group in 2-methyl-3-amino-4-quinazalone exhibits a marked decrease in reactivity as chloral condenses with it to give the intermediate 2-methyl-3- β -trichloro- α -hydroxyethylamino-4-quinazalone (IV). Chloral could not be further condensed with the 2-methyl group due to the steric hindrance. On acetylation, the α -hydroxy group instead of forming the regular acetyl derivative eliminates water similarly giving 2-methyl-3-trichloroethylideneamino-4-quinazalone. The alkaline hydrolysis product of (IV) is under investigation.

EXPERIMENTAL.

2- γ -Trichloro- β -hydroxypropyl-4-quinazalone. —2-Methyl-4-quinazalone (10 g.) and chloral (10 g.) were heated in a flask, fitted with an air-condenser, on a wire-gauge over a low flame for 3 hours. On cooling, the mixture was poured into water and allowed to stand till the pasty mass solidified (15 g.). It crystallised from rectified spirit in shining yellow needles, m. p.

204-5°. It readily dissolves with decomposition in cold caustic alkali. It also dissolves in slightly warm dilute hydrochloric acid. It gives greenish fluorescence with dilute alcohol. (Found: C, 42.7; H, 2.9; N, 8.8; Cl, 34.53. $C_{11}H_9O_2N_2Cl_3$ requires C, 42.9; H, 2.9; N, 9.1; Cl, 34.63 per cent). Hydrochloride of 2- γ -trichloro- β -hydroxy-4-quinazolone does not melt at 300°. (Found: Cl, 41.0. $C_{11}H_{10}O_2N_2Cl_4$ requires Cl, 41.2 per cent).

3 *4-Dihydro-4-keto-2-quinazolinyl-trichloropropylene*.—A mixture of the above compound (2 g.) and acetic anhydride (2 c.c.) to which one drop of concentrated sulphuric acid had been added was warmed in a test tube fitted with a condenser for 2 hours. On cooling, the mixture was poured into water, when a solid separated out. It crystallised from glacial acetic acid in white granules, m. p. 212°. It is insoluble in alkali and hydrochloric acid. (Found Cl, 36.4. $C_{11}H_7ON_2Cl_3$ requires Cl, 36.8 per cent).

4 *Quinazolone-2-acrylic acid*.—2- γ -Trichloro- β -hydroxy-propyl-4-quinazolone (5 g.) was dissolved in sodium hydroxide (10%, 50 c.c.) and the solution heated at 60° on a water-bath for $\frac{1}{2}$ hour. On cooling it was neutralised to slight acidity by dilute acetic acid and the solution was concentrated to half the volume. The product crystallised on keeping in frigidaire in yellowish prismatic crystals, m. p. 262-63°. It is strongly acidic to litmus and gives effervescence with dilute sodium bicarbonate solution. (Found: C, 60.6; H, 3.9; N, 12.8. $C_{11}H_8O_3N_2$ requires C, 61.1; H, 3.7; N, 13.0 per cent).

2 *Methyl-3- β -trichloro- α -hydroxyethylamino-4-quinazolone*.—2-Methyl-3-amino-4-quinazolone (5 g.) and chloral (4 g.) were mixed together in a flask fitted with an air-condenser; when the mixture became hot. This mixture was heated on a water-bath at 70°-80° for 1 hour and on cooling, was poured into water. It crystallised from alcohol in white shining needles, m. p. 151-52°. (Found: N, 13.2; Cl, 33.3. $C_{11}H_{10}O_2N_3Cl_3$ requires N, 13.0; Cl, 33.0 per cent).

2 *Methyl-3-trichloroethylideneaminoquinazolone*.—2-Methyl-3- β -trichloro- α -hydroxyamino-4-quinazolone (1.5 g.) was dissolved in pyridine (10 c.c.) and acetyl chloride (2 c.c.) was added to it gradually at 0° with constant stirring. It was kept in a refrigerator overnight. Next day the solution was poured into dilute hydrochloric acid when a solid separated out. It crystallised from alcohol in white needles, m. p. 104°-5°. (Found: N, 13.8. $C_{11}H_8ON_3Cl_3$ requires N, 13.8 per cent).

THE FATTY OIL FROM THE SEEDS OF *PRINSEPIA UTILIS*, ROYLE.

BY S. V. PUNTAMBEKAR.

The chemical and physical constants of the fatty oil (21%) from the seeds of *Prinsepia utilis*, Royle as well as of its constituent acids have been determined. No constituent of medicinal value has been located in the oil.

Prinsepia utilis, Royle (N.O. Rosaceae) known as *bhekal* (Hind.) is a deciduous, thorny shrub found in the outer Himalayas, from Hazara to Bhutan at 2,000 to 9,000 ft. It also occurs in Khasia Hills and is naturalized in the Nilgiris. The fruit is 0.5"—0.7" long, cylindrical, fleshy and deep purple when ripe and has one seed. By expression the seeds yield a fatty oil which is much used in the N. W. Himalayas for food, illumination and as a medicine.

Except for the statement made by Kirtikar and Basu ("Indian Medicinal Plants," 1st Ed., Pt. I, p. 521) that "In specific gravity, iodine value and melting point of the insoluble fatty acids, the oil (two samples at Indian Museum) resembles that derived from cotton seed", there is no reference in literature to the physical and chemical properties of the oil. It was, therefore, thought advisable to record the results of the detailed examination of the oil in this paper.

E X P E R I M E N T A L.

The air-dried seeds (received from the Divisional Forest Officer, Chakrata Forest Division, Chakrata, U. P.) were found to consist of 37.5% pericarp and 62.5% kernels. The latter on hot expression in a hydraulic press yielded 18% of a pale yellow fatty oil. Additional 19.2% were obtained by extraction of the residual cake with petroleum ether thus making a total of 37.2%.

TABLE I.
Chemical and physical constants.

| Fatty oil | | | | Mixed acids | |
|----------------------------|------------|---------------|-------|-------------------------|-----------|
| Consistency | ... Thin | Sap. value | 200.2 | Mean M. W | ... 272.3 |
| Rotation $[\alpha]_D^{30}$ | .. Nil | Acid value | 23.1 | Iodine value (Hanus) | ... 112.0 |
| Sp. gr. at 20° | ... 0.9215 | Acetyl value | 12.3 | Sat acids | .. 21.3% |
| Ref. index at 20° | ... 1.4625 | Hehner value | 89.3 | Unsat. acids | . 77.2% |
| Iodine value* (Hanus) | ... 109.8 | Unsap. matter | 0.5% | Resin acids | .. 1.5% |

* On standing the oil got oxidised and in course of a year the iodine value fell to 84.0.

Composition of the Mixed Acids.

The oil (285 g.) was saponified with alcoholic sodium hydroxide. The alcohol was distilled off, the resultant soap dissolved in water and the mixed acids liberated by the addition of concentrated hydrochloric acid. The free fatty acids were washed with warm water and neutralised with 10% sodium hydroxide. The soap solution was concentrated, incorporated with washed filter paper pulp and the resulting mass was dried, powdered, and extracted with ether in a soxhlet to remove the unsaponifiable matter. The mixed acids (204 g.) were liberated from the residual soap, purified in the usual manner and 147.5 g. of these were separated into solid and liquid acids by the well known Twitchell's lead salt-alcohol method (*Ind. Eng. Chem*, 1921, 13, 806).

TABLE II.

| | Acids | Net wt. | I. V. |
|-----|--------|--------------|-------|
| (S) | Solid | 28.70 | 2.3 |
| (S) | Solid | 5.58 | 31.6 |
| (L) | Liquid | 111.20 | 142.3 |
| (R) | Resin | 2.02 | — |
| | | <hr/> 147.50 | |

Solid Acids (S).

The solid acids (44 g.*) were converted into methyl esters in the usual manner with 3% methyl alcoholic hydrochloric acid. After distilling off the methyl alcohol the esters were washed with saturated salt solution, 5% sodium carbonate and finally with distilled water. After drying under vacuum 42 g. of the esters were distilled at 9 mm. into the following fractions.

TABLE III.

| Fractions | B p. | Mean M. W. | Net wt. | Component methyl esters | | | |
|----------------|------------|------------|---------|-------------------------|------------|----------|--------------|
| | | | | Myristate. | Palmitate. | Stearate | Lignocerate. |
| S ₁ | Below 185° | 240.1 | 0.75 | 0.75 | — | — | — |
| S ₂ | 185°—188° | 268.2 | 3.10 | — | 3.10 | — | — |
| S ₃ | 188°—191° | 270.0 | 14.50 | — | 14.50 | — | — |
| S ₄ | 191°—193° | 276.5 | 8.84 | — | 6.79 | 2.05 | — |
| S ₅ | 193°—199° | 280.8 | 5.60 | — | 3.44 | 2.16 | — |
| S ₆ | 199°—205° | 283.4 | 3.29 | — | 1.72 | 1.57 | — |
| S ₇ | 205°—210° | 298.2 | 3.52 | — | — | 3.52 | — |
| Residue | — | — | 2.40 | — | — | 0.40 | 2.00 |
| | | Total | 42.00 | 0.75 | 29.55 | 9.70 | 2.00 |
| | | Per cent | 100% | 1.8% | 70.3% | 23.1% | 4.8% |

* A portion was taken from a separate Twitchell's separation.

All these fractions were saponified separately, the corresponding acids were liberated and these were fractionally crystallised from acetone in order to isolate the individual acids in the usual manner.

Acids from fraction S_1 had a mean M. W. of 226.1 and melted at 50-51°. The acid, therefore, appears to be myristic. The quantity being small no further identification was possible.

Acids from fraction S_2 (m.p. 58-59°, mean M. W. 259) and S_3 (m.p. 58-59°, mean M. W., 258.6) being alike were mixed together and crystallised from dilute acetone. Crystals, m.p. 61-62°, M. W. 258, were obtained. Their mixed melting point with an authentic sample of palmitic acid remained unaltered. The residue from the mother-liquor melted at 59-60° and had a M. W. of 260. The fractions thus almost entirely consisted of palmitic acid.

Acids from fractions S_4 and S_5 were separately obtained and fractionally crystallised from acetone. Products melting at 57-58° and 56-57° and having M. W. 262.5 and 266.8 were obtained. Further crystallisation did not bring about separation of any acid but gave the same product, m.p. 54-55°, M. W. 269. This was presumably the eutectic mixture of palmitic and stearic acid since palmitic acid was found in fraction S_3 and stearic in fraction S_6 .

Acids from fraction S_6 had a melting point of 58-59° and M. W. of 269.4. Crystallised from acetone crystals melting at 66-67° (mixed m.p. with pure stearic acid 67-68°) and M. W. 278.2 were obtained. The fraction thus contains stearic acid (isolated) and palmitic acid (not isolated).

Acids from fraction S_7 melted at 64-65°. Their mixed melting point with a sample of pure stearic acid was 64-66°. Twice crystallised from alcohol they melted at 68-69°, M. W. 284.2. Their mixed melting point with pure stearic acid remained unaltered. The acids from the mother-liquor melted at 64-65°, M. W. 280.0. The acids from this fraction consisted almost entirely of stearic acid.

The acids from the residue being mixed with the products of decomposition were highly coloured. These were first saponified and the liberated acids were thrice crystallised from dilute acetone giving crystals, m.p. 75-76°, M. W. 358.4. When mixed with a pure sample of lignoceric acid the melting point was 77-78°. The acid thus appeared to be lignoceric acid. The residue from mother-liquor on concentration and crystallisation yielded crystals melting at 64-65°, M. W. 310.9. Mixed m.p. with pure stearic acid was 64-67°. The residue, therefore, appeared to consist of lignoceric and stearic acids.

Solid Acids (S').

These acids were liberated from the lead salts that had crystallised out on standing from the lead salts of liquid acids after the latter's separation by Twitchell's method. They were oxidised according to the method of Bertram (*Zeit. deut. oel fett Ind.*, 1925, **46**, 733) to remove the unsaturated acids. The resulting saturated acids (M. W. 245) on crystallising twice from dilute acetone gave a product, m.p. 58-59°, M. W. 259. Its mixed melting point with pure palmitic acid was 61-63°. From the filtrate a product melting at 50-51° presumably myristic acid was isolated but was not sufficient for further identification. These solid acids, therefore, consisted of a mixture of myristic, palmitic and unsaturated acids identified below.

Liquid Acids (L).

Oxidation.—The liquid acids were saponified to break up any esters which might have been formed during Twitchell's separation. A portion of the de-esterified acids was converted into potassium soap and oxidised in cold alkaline solution with dilute potassium permanganate according to the modified method of Hazura (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", 1921, 6th Ed., Vol. I, p. 575). From the resultant acids dihydroxystearic acid, m.p. 130-31°, M. W. 315, a tetrahydroxy stearic acid (sativic acid) m.p. 172-75°, M. W. 352, and azeleic acid, m.p. 101-102°, M. W. 186.5, were isolated. No hexahydroxystearic acid was found indicating thereby the absence of linolenic acid.

Bromination.—Liquid acids (2.6502 g.) were brominated according to the method of Eibner and Muggenthaler (Lewkowitsch, *loc. cit.* p. 585) yielding 3.9200 g. of the brominated product but no hexa or higher bromides. The product was soluble in petroleum ether and no crystalline tetrabromide could be isolated on concentrating and cooling the solution. This showed that the terabromides present were mostly from β -linoleic acid. The oxidation and the bromination results thus clearly showed that the liquid acids consisted only of oleic and linoleic acids.

The above data on calculation gave the percentages of the constituent acids as follows: myristic (1.8%), palmitic (15.2%), stearic (4.5%), lignoceric (0.9%), oleic (32.6%), linoleic (43.6%) and resin (1.4%). It may be pointed out here that the mixed fatty acids exhibit the general characteristics of the mixed acids from the seed fats of Rosaceae family (Hilditch, "The Chemical Constitution of Natural Fats", 1940, p. 134) in that the major

component acids are oleic and linoleic and the minor ones palmitic and stearic though palmitic acid occurs in quantity much larger than has so far been found in the family and oleic acid in quantity much smaller.

Unaponifiable Matter.

The unaponifiable matter, obtained from the sodium soaps of the mixed acids by extraction with ethyl ether, when crystallised from alcohol gave plates, m.p. 127-28°. On recrystallisation from the same solvent crystals melting at 128-29° were obtained. The acetyl derivative of the product melted at 118-19°. The product gave the usual tests for phytosterol and appeared to be sitosterol, the common phytosterol found in seed fats.

C O N C L U S I O N.

The fatty oil from the seeds of *Prinsepia utilis*, Royle, consists of the glycerides of myristic acid (1.8%), palmitic acid (15.2%), stearic acid (4.5%), lignoceric acid (0.9%), oleic acid (32.6%) and linoleic acid (43.6%) together with resin acid (1.4%) and unaponifiable matter (0.5%), containing the sterol, sitosterol. There is nothing out of the ordinary in the composition of the oil to explain its supposed medicinal properties. It might, however, be said that the oil belongs to the semi-drying class and can be used for edible purposes and in soap making.

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A NOTE ON THE UNRELIABILITY OF THE RESORCINOL-PERIODATE TEST FOR HYPONITRITES

BY W. V. B. SUNDARA RAO AND V. V. K. SASTRY.

Corbet (*Biochem. J.*, 1940, **34**, 1019) refuting the criticism of Rao *et al* (*J. Indian Chem. Soc.*, 1938, **15**, 599) regarding the reliability of his resorcinol-periodate test (Corbet, *Biochem. J.*, 1934, **28**, 1575) for hyponitrite, reasserts without giving any details of the method employed by him that the test is useful for distinguishing between hyponitrite and nitrite. In view of this confused position in literature it has been felt desirable to examine and see the reliability or otherwise of this test.

The test solution of hyponitrite was prepared according to the method suggested in Mellor's "Treatise of Inorganic Chemistry" (1928, VIII, p. 405). Freshly prepared solutions of resorcinol ($M/5$) and sodium periodate (saturated) were employed as reagents.

In a neutral or slightly alkaline medium a light pink colour is given not only by hyponitrite, hydroxylamine, borate and bicarbonate, as pointed by Corbet, but by nitrite and nitrate as well, down to a concentration of ten parts per million. Between p_H ranges 1-3, hydroxylamine, hyponitrite and nitrite give an intense cherry-red colour, the intensity of the colour varying with the concentration. The concentration of nitrite should not, however, be more than 1,000 p.p.m., while at p_H 4 the cherry-red colour is not produced till after 30 minutes, at p_H 5 and 6 this colour is not formed. At p_H 7 and 8 a light pink colour is formed, while in strongly alkaline solutions a yellowish green colour is produced which becomes red on acidification. It has been found that the buffers (Rao *et al*, *loc. cit.*) by themselves do not give any colour with the reagents and the excess of sodium chloride before or after the addition of the reagents has no effect. Hence the buffers employed and excess of sodium chloride present along with the hyponitrite have no effect on the production of the colour. Also varying the concentration of the resorcinol or the order of the addition of the reagents or using a mixture of them, has no effect on the colour formation. Therefore, in view of the similarity in production of colour, the test is unreliable and as such is not useful for distinguishing between hyponitrite and nitrite.

Our thanks are due to Rao Bahadur B. Viswanath and Dr. S. V. Desai for their keen interest in this piece of work.

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VARIATION IN THE ELECTROCHEMICAL PROPERTIES OF HYDROGEN CLAY SOLS WITH TEMPERATURE.*

BY B. CHATTERJEE AND A. SEN.

In a previous note (Chatterjee and Sen, *J. Indian Chem. Soc.*, 1941, 18, 646) it has been observed that a hydrogen clay sol H[†] shows an increase of its free acidity from $0.96 \times 10^{-5}N$ to $2.5 \times 10^{-5}N$ when the temperature is raised from 1° to 50° but gives a constant total acidity ($286 \times 10^{-5}N$) at these temperatures. Results with another hydrogen clay sol Padegaon-B[†] are given in this note (Table I) which show the free acidity, the total acidity and the degree of dissociation all increase with a rise of temperature.

TABLE I.

Colloid content = 3.51 g. per litre.

| Free acidity $\times 10^6N$ | | | Total acidity $\times 10^6N$. | | | Degree of dissociation (%) | | | p_H at inflexion. | | |
|-----------------------------|-----|-----|--------------------------------|-----|-----|----------------------------|-----|-----|---------------------|------|------|
| 1° | 35° | 50° | 1° | 35° | 50° | 1° | 35° | 50° | 1° | 35° | 50° |
| 1.1 | 5.0 | 7.9 | 200 | 235 | 252 | 0.5 | 2.1 | 3.1 | 9.15 | 8.15 | 7.75 |

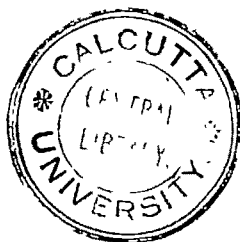
The inflexion points become displaced to lower p_H values with increasing temperatures. It is interesting to note that while the total acidity of the hydrogen clay sol H remains constant at different temperatures, that of Padegaon-B increases with increasing temperatures. In view of the differences between the two clays, these temperature variations are being studied further.

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† Sols H and Padegaon-B were prepared respectively from the entire clay fractions of a neutral calcareous soil from the Government Seed Farm, Kalyanpore (U. P.) collected from a depth of 0 to 6 inches and a non-lateritic calcareous soil, B-type from Padegaon (Nira, Poona) Farm collected at a depth of 0 to 12 inches.



PROPERTIES OF DIALYSED HYDROUS ALUMINA HYDROSOLS. PART II. TITRATION WITH BASES AND ACIDS.

BY N. P. DATTA.

Potentiometric titrations have been carried out with acids and bases. Buffering is maximum at p_H 11.2 with NaOH; at p_H 11.0 with $Ba(OH)_2$ and at p_H 10.8 with $Ca(OH)_2$. A weak inflexion point has been observed at p_H 12.2 and the buffer index curve shows a minimum at this point. The amount of alumina coming into true solution increases with the concentration of alkali and complete solution occurs at the inflexion point at p_H 12.2. Titration of aluminium chloride with NaOH shows an inflexion near p_H 11.0 corresponding to the complete solution of precipitated alumina. The p_H at which this inflexion point occurs, however, depends on the age of the precipitate. HCl is totally adsorbed at small concentrations. A strong buffer action indicating true solution is observed at p_H 3.5, 3.4, 3.0 and 2.8 for acetic, phosphoric, oxalic and sulphuric acids respectively.

There is some difference of opinion as to whether a solution of aluminium hydroxide in alkalis is to be regarded as a case of true solution or of peptisation (Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 864; Blum, *ibid.*, 1913, **35**, 1499; Britton, *J. Chem. Soc.*, 1925, **127**, 2120; Miller, *Colloid Symposium Monograph*, 1925, **3**, 208; Mahin, Ingraham and Stewart, *J. Amer. Chem. Soc.*, 1913, **35**, 30; 1914, **36**, 2381; Davis and Farnham, *J. Phys. Chem.*, 1932, **36**, 1057; Dhar and Chatterji, *Chem. News*, 1920, **121**, 253). In the present paper colloidal hydrous alumina and aluminium chloride solutions have been titrated potentiometrically with bases-NaOH, $Ba(OH)_2$, $Ca(OH)_2$ and $Mg(OH)_2$ and acids-HCl, H_2SO_4 , H_3PO_4 , $H_2C_2O_4$ and CH_3COOH .

EXPERIMENTAL.

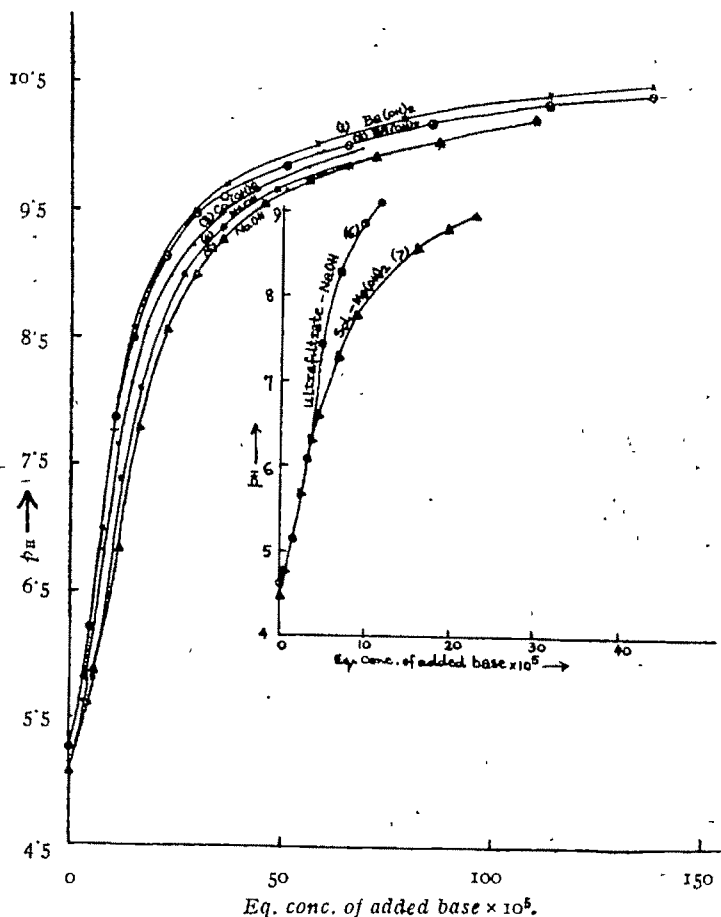
The preparation of the sols and the experimental technique used have been described in Part I (*J. Indian Chem. Soc.*, 1942, **19**, 159). Duplicated titrations show good agreement (Fig. 1, curves 1 and 2, 4 and 5; Fig. 2, curves 8, 9, 10 and 11). For ultrafiltration perforated porcelain bed and 'cella' finest membranes have been used. Aluminium has been estimated in the ultrafiltrates according to the method of Berg (*Z. anal. Chem.*, 1927, **71**, 369) by 8-oxyquinoline. A water thermostat has been used at $35 \pm 0.05^\circ$.

Titration with Bases.

The sols used in this work are the same as have been described in Part I. The results are given in Figs. 1—4. On the addition of a base the p_H increases at first very sharply but thereafter its change indicates a strong buffer action. Sol A (Fig. 1, curves 1 and 2) shows a weak inflexion point at p_H 6.2 which should be attributed to dissolved hydrochloric acid or adsorbed aluminium chloride and the titration curve of its

FIG. 1.

Hydrous alumina sol A—titration with bases.

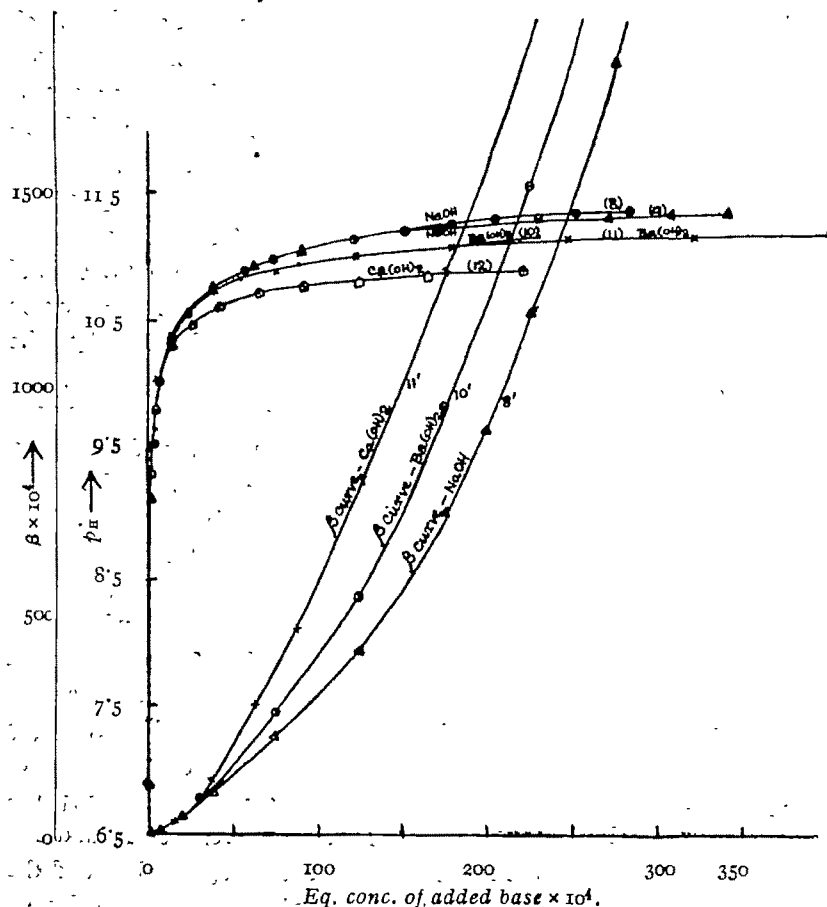


ultrafiltrate with NaOH (Fig. 1, curve 6) gives a total acidity of $3 \times 10^{-5}N$. Strong buffering is observed near p_H 11.25 with NaOH, at p_H 11.0 with $Ba(OH)_2$, and at p_H 10.8 with $Ca(OH)_2$ (Fig. 2). With NaOH a weak

inflexion point and complete solution of alumina has been obtained by proceeding up to p_H value as high as 12.5 (Fig. 3, curve 13). But no such inflexion point and complete solution has been observed with $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, probably because very high p_H values could not be reached with these bases. The buffer indices for sol C are plotted in curves 8', 10' and 11' of Fig. 2. The buffer index rises slowly at first then rapidly and assumes infinite values indicating a very strong buffer action. In the case of NaOH (Fig. 3, curve 13') it is finally followed by a minimum indicating an inflexion corresponding to the neutralisation of an acid.

FIG. 2.

Hydrous alumina sol C—titration with bases.



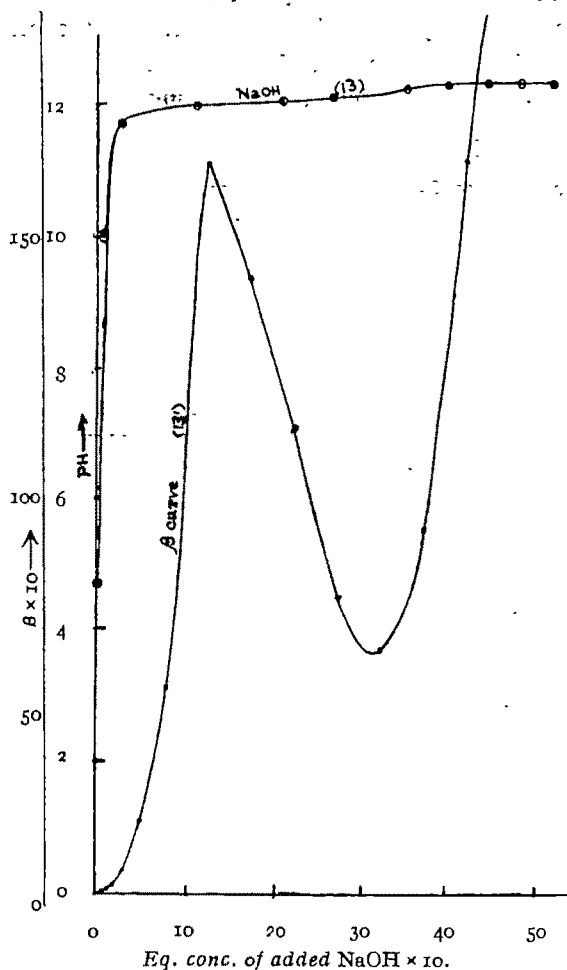
Rabinowitsch and Wassiliev (*Kolloid Z.*, 1931, 56, 305) titrated aluminium hydroxide sols with KOH but the p_H at the horizontal part and the p_H at the inflexion point in their curve are different from those of the

curves given in this paper. It will be shown later that precipitates of the different 'age' show a difference in this p_H value.

Solutions of aluminium chloride have also been titrated with NaOH. The

FIG. 3.

Hydrous alumina sol B.



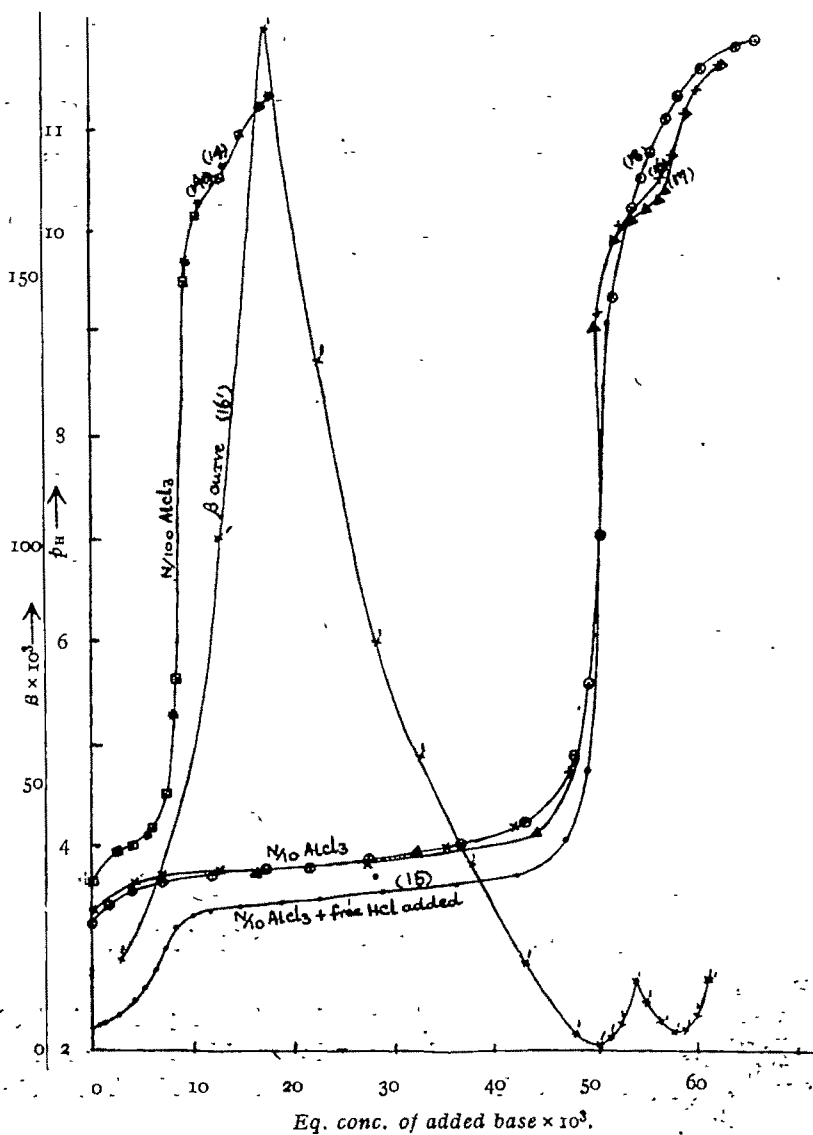
results given in Fig. 4 show that the curves are of the same form as those obtained by Britton (*loc.cit.*) and Davis and Farnham (*loc.cit.*) but differ from those of Hildebrand (*loc.cit.*) and of Blum (*loc.cit.*) which have a weak inflexion point in their initial portion. Davis and Farnham (*loc.cit.*) ascribe this inflexion point to the free acid contained in the solutions used by them. Their opinion is confirmed by the titration curve (Fig. 4, curve 15) of an aluminium chloride solution to which some free acid has been added. On the addition of alkali the p_H at first rises sharply and when particles of alumina appear, the p_H remains almost constant between 3.5 and 4.0 as long as

alumina continues to be precipitated. This p_H of precipitation depends on the initial p_H of the $AlCl_3$ solution (Fig. 4, curves 16, 17 and 18). When all the alumina has been precipitated, the p_H again rises and the titration curve shows a sharp inflexion at p_H about 7.6. A second inflexion point corresponding to the solution of alumina is observed at p_H about 10.9. It has been found that alumina precipitated by small additions of alkali inside the titration cell when kept for sufficient time (about 12 hours) cannot

be easily dissolved even with larger concentration of alkali (Fig. 4, curve 18). The titrations were therefore carried out by measuring the p_H of a definite volume of the sol contained in separate Jena glass bottles to which increasing amounts of alkali had been added.

FIG. 4.

$AlCl_3$ solution—titration with $NaOH$.



Aluminium has been estimated in the ultrafiltrates of sol C corresponding to different stages in its titration with bases. Results are given in Table I.

TABLE I.

Sol C. (20 c.c. of sol = 25.5 mg. of Al_2O_3).

| Sodium hydroxide. | | | Barium hydroxide | | |
|-------------------------|---------|---------------------------|-------------------------|---------|---------------------------|
| Conc. of alkali. | p_H . | Amount in 20 c.c. of sol. | Conc. of alkali | p_H . | Amount in 20 c.c. of sol. |
| $10.95 \times 10^{-3}N$ | 11.35 | 0.65 mg. | $11.65 \times 10^{-3}N$ | 11.54 | 0.04 mg. |
| 33.45 | 11.97 | 1.65 | 21.71 | 11.84 | 0.13 |
| 42.95 | 12.09 | 3.80 | 51.14 | 12.20 | 0.29 |
| 50.04 | 12.19 | 4.20 | 70.09 | 12.25 | 0.43 |
| 55.40 | 12.23 | 4.82 | | | |

The amount of alumina coming into solution increases as the p_H rises but more so for NaOH than for $\text{Ba}(\text{OH})_2$ compared at the same p_H .

Hildebrand (*loc. cit.*) and Blum (*loc. cit.*) titrated aluminium sols with alkalis and obtained an inflexion point near p_H 11.0 at which p_H they found that the solution was free from particles of colloidal dimensions. They concluded that a definite compound namely NaAlO_2 was formed. Britton (*loc. cit.*) also considers this inflexion point to denote the formation of aluminates. Mahin, Ingraham and Stewart (*loc. cit.*) hold that the colloidal properties of aluminium hydroxide play such an important part in conditioning its solubility in bases that there is room for doubt whether the alleged aluminates exist as definite salts at all. Dhar and Chatterji (*loc. cit.*) observed that the conductivity of a solution of sodium hydroxide was not appreciably changed by the addition of aluminium hydroxide and concluded that the formation of these solutions were cases of peptisation and not of chemical dissolution. Davis and Farnham (*loc. cit.*) do not consider the inflexion points in the titration curves with alkalis as decisive evidence of the formation of aluminates and consider peptisation by hydroxyl ions to be responsible for the solution.

The ultrafiltrates of solutions at or beyond the inflexion point, obtained with or without addition of sodium and magnesium sulphates in sufficient quantities were analysed and their aluminium content estimated. The results are given in Table II.

TABLE II.

| System. | Amount of alumina in 25 c.c. |
|--|---------------------------------|
| AlCl ₃ solution ... | 0.045 g. |
| " ... | 0.046 |
| Ultrafiltrate of AlCl ₃ solution (25 c.c.) + 51 c.c. 0.99 N/10-NaOH | 0.045 |
| Ultrafiltrate of AlCl ₃ solution (25 c.c.) + 51 c.c. of 0.99 N/10-NaOH + 2g. of Na ₂ SO ₄ | 0.045 |
| Ultrafiltrate of AlCl ₃ solution (25 c.c.) + 60 c.c. of 0.99 N/10-NaOH | 0.045 |
| Ultrafiltrate of AlCl ₃ solution (25 c.c.) + 60 c.c. of 0.99 N/10-NaOH + 4g. of Na ₂ SO ₄ | 0.046 |
| Ultrafiltrate of AlCl ₃ solution (25 c.c.) + 60 c.c. of 0.99 N/10-NaOH + 4g. of MgSO ₄ | 0.045 |

The ultrafiltrate revealed no particles when examined in the ultra-microscope, the alumina coming into the ultrafiltrate was invariably equal to the total quantity of alumina present in the aluminium chloride solution. The addition of Na₂SO₄ rules out the possibility of colloidal particles passing through the ultrafilter membrane and the results prove definitely that true solution of alumina takes place at this inflexion point.

As already mentioned, the first and the second inflexion points in the titration of solutions of aluminium chloride with NaOH correspond respectively to the precipitation and solution of alumina by the alkali. The amount of alkali (3.73 c.c. of 0.099N) required between these two inflexion points therefore has reacted with alumina (0.0184 g.) precipitated from 10 c.c. of aluminium chloride solution used. The calculated molar ratio of Al₂O₃ : NaOH is 2.05. The composition of aluminate therefore appears to be Al₂O₃.2NaOH or NaAlO₂, neglecting the difference, which is within the experimental error, of the value 2 from the experimental value 2.05.

Titration with Acids.

With Hydrochloric Acid.—Hydrous alumina sols A and C have been titrated with hydrochloric acid and the p_H , specific conductivity and chloride ion activity measured. The results for sol A are given in curves 19 and 20 (Fig. 5) and those for sol C in curves 29, 29a, 30 and 31 (Fig. 7). Titrations of HCl solutions having nearly the same p_H as that of sol have also been carried out for comparison. The results are given in curve 28 of Fig. 7. It will be found that the p_H (Fig. 5, curve 19; Fig. 7, curves 29, 30, 31), specific conductivity (Fig. 5, curve 20) and chloride ion activity (Fig. 7, curve 29a) of sols remain unchanged in the initial stage of the titra-

tion indicating that both hydrogen and chloride ions completely disappear by reaction with the surface of the colloid particles and no increase in the concentration of free ions takes place. On larger additions, the p_H decreases and the specific conductivity and the chloride ion activity increase. Table III gives the amount of HCl thus adsorbed in the initial stages of the titration during which the curves remain more or less flat.

FIG. 5.

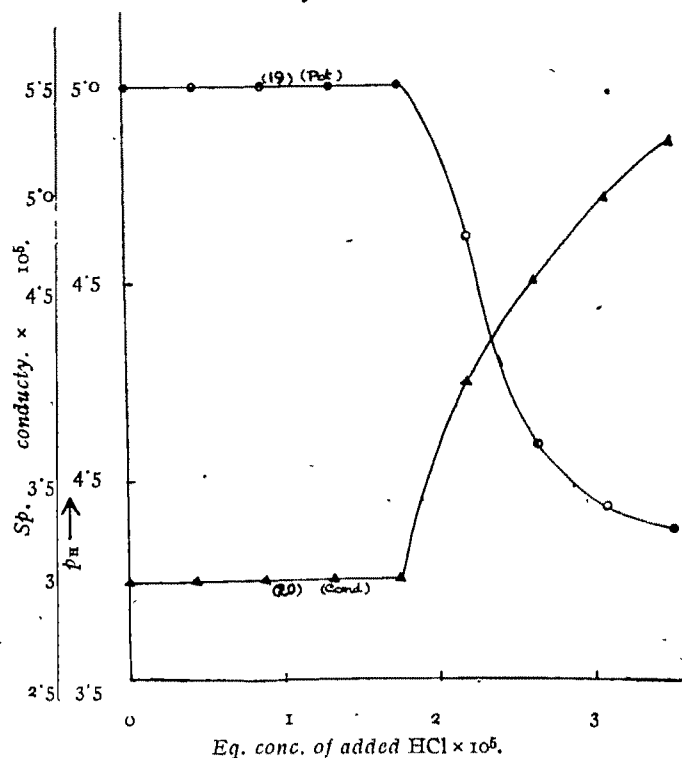
Hydrous alumina sol A.

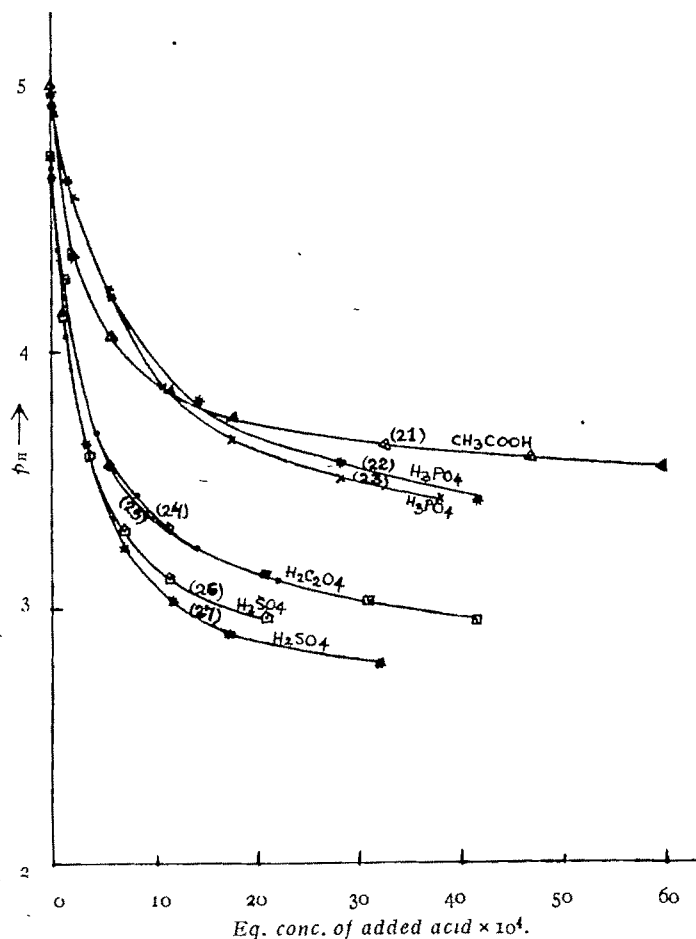
TABLE III.

| Sol | Alumina content. | Curve No. | Number of moles (mean of HCl adsorbed per g. mol. alumina). |
|-----|--------------------------------------|------------|---|
| A | 1.37×10^{-3} g. moles/litre | 19 (pot.) | 0.127×10^{-3} |
| | | 20 (cond.) | 0.127 |
| C | 1.25×10^{-3} g. moles/litre | 29 (pot.) | 0.40 |
| | | 30 (pot.) | 0.32 |
| | | 31 (pot.) | 0.32 |

The amount of HCl thus taken up amounts to only a very small percentage of the alumina present, but differs considerably for the two sols which is to be expected if it resulted from a surface reaction. The reaction of the sol with HCl may be looked upon as the adsorption of both H^+ and Cl^- ions in the double layer. This aspect has been discussed in Part I. According to this view aluminium hydroxide particles contain both the cation Al^{+++} and the anion AlO_2^- on their surface as the primarily adsorbed ions. The two kinds are in equilibrium, their relative proportions

FIG. 6.

Hydrous alumina sol A—titration with acids.

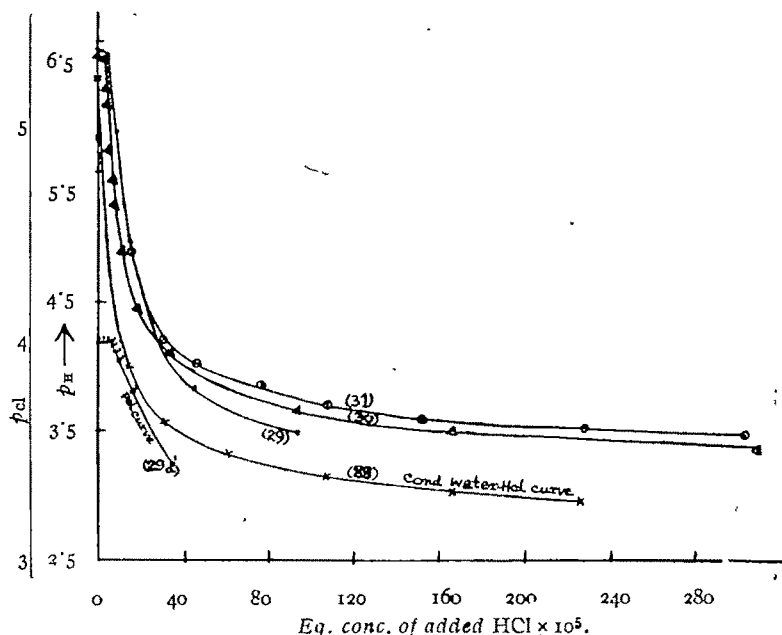


depending on the p_π of the system. With each addition of HCl, a new equilibrium between them is set up and further, some of the Cl^- ions and

of the excess of H^+ ions are electrically adsorbed respectively on the Al^{+++} and AlO_2^- ions on the surface. The adsorbed Cl^- ions also displace some of the OH^- ions into the solution which again neutralise the remaining H^+ ions. It appears that in the initial stages of the titration, the added H^+ and Cl^- ions disappear from the solution in this manner. The result is

FIG. 7.

Hydrous alumina sol C—titration with HCl

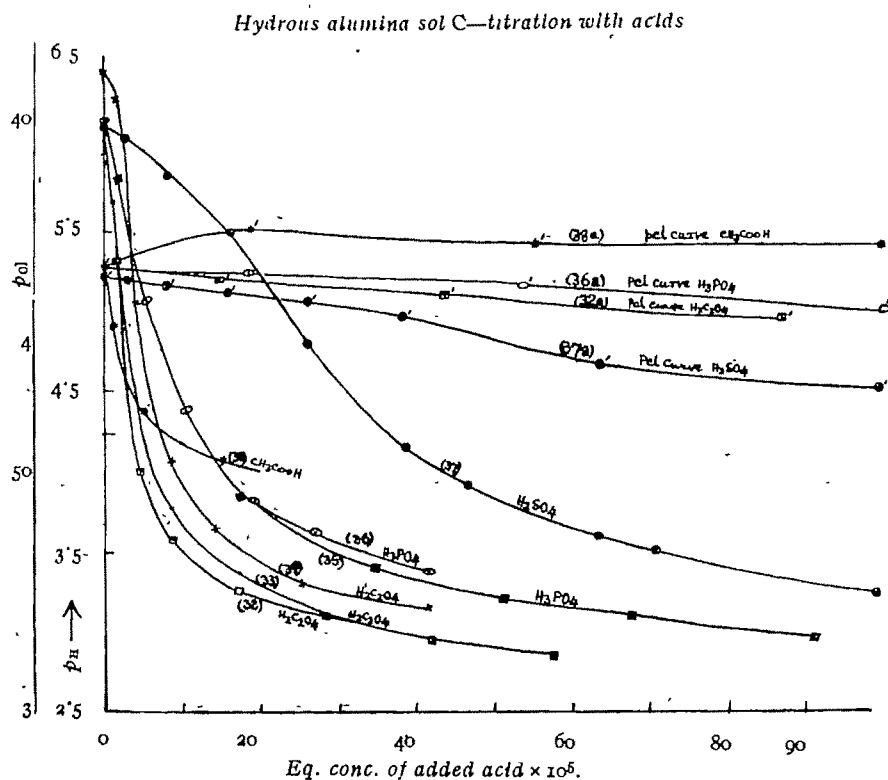


interesting in connection with the study of the toxic effect of aluminium ions in acid soils. It shows that aluminium hydroxide in the colloidal state can react with H^+ ions at a p_H as high as 6.2. At higher concentrations a gradual dissolution of the particles sets in. A strong buffering is indicated near about p_H 3.5 (sol C, Fig. 7, curves 29, 30, 31). Aluminium chloride solutions with NaOH (Fig. 4, curves 16, 17, 18) also show a similar buffer action at almost the same p_H region (3.5–4.0) caused by the precipitation of the hydroxide. Dilute HCl having almost the same p_H as that of the sol also shows a strong buffering (Fig. 7, curve 28) but this is at a lower p_H (3.0). Silicic acid sol, when titrated with HCl, shows a buffering between p_H 2.5 and 3.0 (B. Chatterjee, *Proc. Indian. Sci. Cong. Assoc.*, 1942, III). Pauli and Schmidt (*Z. physikal. Chem.*, 1927, 129, 199) also found that alumina sol takes up HCl at first rapidly then slowly up to about 18%,

of the alumina present. They regarded the remaining 82% as the 'neutral colloid' which is inert. But from what has been said above, the adsorption of HCl by alumina appears to be a reaction on the surface and not a chemical one with a fraction of the colloid particles.

With Acetic, Oxalic, Sulphuric and Phosphoric Acids.—Sols A, B and C have been titrated with solutions of the above acids. The results are expressed for sol A in Fig. 6; curve 21 for acetic acid; curves 24, 25 for oxalic acid; curves 26, 27 for sulphuric acid; curves 22, 23 for phosphoric acid; and for sol C in Fig. 8, curves 32, 33, 34 for oxalic acid; curves 35, 36 for phosphoric acid; curve 37, for sulphuric acid and curve 38 for acetic acid. It will be found that the p_H decreases at first rapidly, then slowly and

FIG. 8.



ultimately reaches almost a constant value indicating strong buffer action. Buffering occurs at about p_H 3.5 for acetic acid; at about p_H 3.4 for phosphoric acid; at about p_H 3.0 for oxalic acid and at about p_H 2.8 for sulphuric acid. Measurements of the chloride ion activity of the sol (Fig. 8, curves 32a, 36a,

37a, 38a) show that all of these acids excepting acetic acid displace Cl^- ions into solution. The order of the acids in the displacement of chloride ions from the micelles by their anions is acetic < phosphoric < oxalic < sulphuric. On the addition of the acids, the anions get adsorbed and displace both Cl^- and OH^- ions into solution but the H^+ ions in solution outnumber the displaced OH^- ions and hence the p_{H} decreases and the chloride ion activity increases. It also shows that the acetate ions at low concentrations are not able to displace chloride ions into solution to a large extent but at large concentration, as is to be expected, some Cl^- ions are displaced. At larger concentrations gradual dissolution of the particles sets in and the p_{H} remains almost constant.

C O N C L U S I O N.

Potentiometric titration of the sols A, C and D with NaOH, $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ have been done. With the exception of a weak inflexion point at a lower p_{H} (6.25) in the case of the titration curves for sol A due to the free acid contained in it, all the titration curves show the same general features. The p_{H} rises sharply, at first to about 10.5 and then remains almost constant indicating a strong buffer action. Buffering is maximum at p_{H} 11.2 with NaOH, at p_{H} 11.0 with $\text{Ba}(\text{OH})_2$ and at p_{H} 10.8 with $\text{Ca}(\text{OH})_2$.

A weak inflexion point has been observed at p_{H} 12.2 and the buffer index curve shows a minimum at this point.

The amount of alumina coming into solution increases with the concentration of alkali and solution occurs at the inflexion point at p_{H} 12.2.

Titration of aluminium chloride with NaOH shows two inflexion points—one at p_{H} 7.6 and the other at p_{H} 10.9—corresponding respectively to the precipitation and solution of alumina by the alkali. The p_{H} of precipitation of alumina depends on the initial p_{H} of the AlCl_3 solution.

The solution of alumina in alkalis has been shown by the estimation of alumina in the ultrafiltrates from the solutions at the second inflexion point and after with or without addition of Na_2SO_4 and MgSO_4 to be a case of true one and not of peptisation as has been supposed by some.

The ratio of Al_2O_3 : NaOH has been found to be 2.05 and hence the composition of sodium aluminate is NaAlO_2 .

HCl at small concentrations is totally adsorbed but this corresponds to only a very small fraction of the alumina present and appears to be a reaction on the surface.

PROPERTIES OF DIALYSED HYDROUS ALUMINA HYDROSOLS 203

A strong buffer action is observed at p_H 3.5, 3.4, 3.0 and 2.8 with acetic, phosphoric, oxalic and sulphuric acids. The acids displace Cl^- ions into solution and the order of them in the displacement of chloride ions by their anions is acetic < phosphoric < oxalic < sulphuric.

Thanks of the author are due to Prof. J. N. Mukherjee for his suggestions and kind interest in the work and to the Calcutta University for the award of a research scholarship during the tenure of which this work was done.

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EFFECT OF LIGHT AND AGEING ON COLLOIDAL SOLUTIONS OF FERRIC HYDROXIDE AND THORIUM HYDROXIDE.

BY R. B. NAIMPALLY, P. M. BARVE AND B. N. DESAI.

Cataphoretic speed, conductivity and stability of colloidal solutions of ferric hydroxide and thorium hydroxide containing different amounts of impurities as brought about by dialysis are found to decrease slowly on exposure to sunlight and on ageing.

In previous papers (Desai and Barve, *Trans. Nat. Inst. Sci. India*, 1939, **2**, 39, Vora, Barve and Desai, *Proc. Indian Acad. Sci.*, 1941, **13**, 100; *J. Bombay Univ.*, 1941, **10**, iii, 40) results of light and ageing on cataphoretic speed, conductivity and stability of colloidal solutions of arsenious sulphide, Prussian blue, gold, vanadium pentoxide, zinc ferrocyanide and ceric hydroxide containing varying amounts of impurities, as brought about by dialysis, have been given. In the present paper similar results obtained with colloidal solutions of ferric hydroxide and thorium hydroxide, whose other properties have already been exhaustively studied in this laboratory, have been presented.

Colloidal solutions of ferric hydroxide (Desai and Borkar, *Trans. Faraday Soc.*, 1933, **29**, 1269) and thorium hydroxide (Desai and Desai, *Trans. Faraday Soc.*, 1934, **30**, 265) were prepared as before and the various experiments performed in the same manner as in the case of colloidal zinc ferrocyanide (Vora, Barve and Desai, *loc. cit.*). All the experiments were carried out at a temperature of 30°. For both the colloidal solutions two samples have been tried (one dialysed for a short period and the other for a long period *i.e.*, before and after the maximum in the cataphoretic speed-dialysis curve is reached, Desai and Barve, *loc. cit.*) in order to note if the amount of impurity in the sol has any effect on the action of light or ageing.

The results are given in Tables I to IV. In all the tables the cataphoretic speed (cat. speed) (mean of direct and reverse movements) is corrected for viscosity and expressed in cm. sec./volt/cm. The stability results (flocculation values—F.V.) are expressed in millimoles of the electrolyte per litre of the mixture (colloid + electrolyte + water).

TABLE I.

Colloidal ferric hydroxide exposed to sunlight.

| Exposure. | Sol dialysed for 4 days | | | Sol dialysed for 20 days. | | |
|-----------|-------------------------|-----------------------|----------------|---------------------------|-----------------------|----------------|
| | Cat. speed. | Sp. condy | F.V. with KCl. | Cat speed. | Sp condy. | F.V. with KCl. |
| 0 hr. | 37.5×10^{-5} | 5363×10^{-6} | 5.10 | 51.8×10^{-5} | 1436×10^{-6} | 1.40 |
| 2 | 34.7 | 5318 | 5.00 | 49.6 | 1396 | 1.36 |
| 4 | 32.4 | 5270 | 4.86 | 47.6 | 1361 | 1.31 |
| 6 | 30.8 | 5217 | 4.68 | 45.8 | 1333 | 1.25 |

TABLE II.

Colloidal thorium hydroxide exposed to sunlight.

| Exposure | Sol dialysed for 4 days | | | Sol dialysed for 20 days. | | |
|----------|-------------------------|-----------------------|----------------|---------------------------|----------------------|----------------|
| | Cat speed | Sp. condy. | F.V. with KCl. | Cat speed | Sp. condy. | F.V. with KCl. |
| 0 hr. | 36.8×10^{-5} | 5047×10^{-6} | 4.70 | 35.4×10^{-5} | 824×10^{-6} | 1.80 |
| 2 | 33.7 | 5025 | 4.52 | 32.3 | 789 | 1.72 |
| 4 | 31.8 | 5011 | 4.38 | 30.3 | 759 | 1.67 |
| 6 | 29.9 | 4982 | 4.15 | 28.8 | 726 | 1.58 |

TABLE III.

Colloidal ferric hydroxide-effect of ageing

| Age. | Sol dialysed for 12 days. | | | Sol dialysed for 20 days. | | |
|--------|---------------------------|-----------------------|---------------|---------------------------|-----------------------|---------------|
| | Cat. speed | Sp. condy | F.V. with KCl | Cat speed. | Sp. condy. | F.V. with KCl |
| 0 days | 67.2×10^{-6} | 3714×10^{-6} | 3.31 | 51.8×10^{-5} | 1436×10^{-6} | 1.40 |
| 31 | 66.5 | 3692 | 3.25 | 51.4 | 1412 | 1.34 |
| 61 | 65.4 | 3648 | 3.21 | 51.1 | 1369 | 1.31 |

TABLE IV.

Colloidal thorium hydroxide-effect of ageing.

| Age. | Sol dialysed for 12 days | | | Sol dialysed for 20 days. | | |
|--------|--------------------------|-----------------------|----------------|---------------------------|----------------------|----------------|
| | Cat. speed | Sp. condy | F.V. with KCl. | Cat. speed. | Sp. condy. | F.V. with KCl. |
| 0 days | 44.3×10^{-5} | 2317×10^{-6} | 3.20 | 35.4×10^{-5} | 824×10^{-6} | 1.80 |
| 31 | 43.5 | 2258 | 3.15 | 34.1 | 794 | 1.77 |
| 61. | 42.1 | 2177 | 3.11 | 33.4 | 767 | 1.72 |

DISCUSSION.

Exposure to Sunlight.—It will appear from the results in Tables I and II that in both cases the cataphoretic speed, conductivity and stability decrease slowly on exposure to sunlight for short period as well as long-period dialysed colloidal solutions. These results are similar to those obtained with colloidal solutions of vanadium pentoxide and can be explained in the same manner (Desai and Barve, *loc. cit.*).

Effect of Ageing.—As in the case of exposure to sunlight, the cataphoric speed, conductivity and stability decrease continuously on ageing (Tables III and IV) of both the short-period and long-period dialysed colloidal solutions of ferric hydroxide and thorium hydroxide. The results can be explained in the same manner as those obtained for vanadium pentoxide (Desai and Barve, *loc. cit.*).

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART IV. THE RELATIONSHIP BETWEEN SOLVENT POWER, GELATION CAPACITY AND VISCOSITY OF SHELLAC SOLUTIONS IN MIXED SOLVENTS.

BY SANTI RANJAN PALIT.

Viscosities of shellac solutions in a mixture of two non-solvents having good solvent power, or of one solvent and another latent solvent have been studied over a wide range of concentration and temperature. The pairs of solvents used are acetone-glycol, methyl acetate-glycol and alcohol-acetone.

Three types of viscosity curves are possible. The position of the minimum in the viscosity curve depends on the temperature and on the concentration of the solute and may vanish above a particular temperature or below a particular concentration. Hence the idea of minimum viscosity signifying maximum solvent power is proved to be fallacious. This is further substantiated by observation of solvent power by the method of precipitation or gelation on cooling. The relationship of the viscosity behaviour with gelation capacity of such systems has been discussed with reference to three-component solubility diagram of such systems.

Indications have been made of a new and rational method of evaluating the solvent power of different solvents for lyophilic solutes.

It has been shown by the author in a previous communication (*J. Indian Chem. Soc.*, 1940, **17**, 663) from a study of shellac solutions in a mixture of acetone and water that when a mixture of two non-solvents forms a good solvent, a minimum in the viscosity-solvent composition curves (to be referred to later as simply viscosity curve) does not occur as a general rule but only under some specified circumstances. The composition corresponding to the viscosity minimum, which according to the current idea (*vide* Mellan's "Industrial Solvents", 1939, Ch. V, p. 64), represents an optimum solvent composition, has been demonstrated to depend considerably on the concentration of the resin and in fact, the minimum has been found to totally disappear below some particular concentration of the resin. In the present paper, the study has been extended to other solvent mixtures to acquire a more extensive knowledge about such behaviour. From a simultaneous study of solubility, viscosity and gel-forming capacity of such systems, important conclusions about the occurrence or non-occurrence of the U-shape of the viscosity curves have been arrived at, and a more thorough understanding and correlation of the solubility behaviour and viscosity of such systems have been secured, which

corroborate the previous results and extend them in some important and fundamental aspects.

EXPERIMENTAL.

The experimental arrangement, procedure, method of expressing concentration, etc., are the same as described in the previous communication. Particular mention should be made of the suitability of Hoesppler falling ball viscosimeter for use with such volatile solvents as acetone, etc. over a wide range of temperature even in conjunction with substances like shellac, nitrocellulose etc. which produce sticky solutions. The ethylene-glycol used is of British Drug House manufacture (ordinary quality) which has been fractionally distilled for purification (191-192° at about 70 cm. atmospheric pressure). Kahlbaum's C. P. quality acetone and Merck's absolute alcohol have been directly used. Methyl acetate (Kahlbaum's ordinary quality) has been dried and fractionally distilled before use.

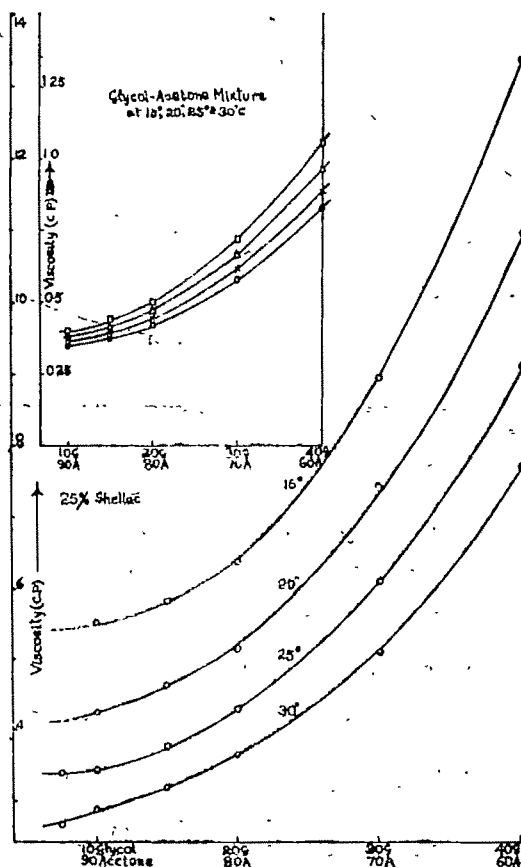
TABLE I.

| Solvent (by wt.) | Viscosity (centipoise) at | | | | Solvent (by wt.) | Viscosity (centipoise) at | | | |
|-----------------------|---------------------------|-------|-------|-------|-----------------------|---------------------------|--------|-------|-------|
| | 15° | 20° | 25° | 30° | | 15° | 20° | 25° | 30° |
| Glycol:acetone. | | | | | Glycol:acetone. | | | | |
| Conc. of shellac=25%. | | | | | Conc. of shellac=35%. | | | | |
| 7'5:92'5 | Pptn | Pptn. | 3'379 | 2'662 | 7'5:92'5 | 25'77 | 13'51 | 9'067 | |
| 10:90 | 5'512 | 4'237 | 3'417 | 2'847 | 10:90 | 21'02 | 13'20 | 9'427 | |
| 15:85 | 5'817 | 4'613 | 3'763 | 3'184 | 12'5:87'5 | 19'68 | 13'32 | 9'687 | |
| 20:80 | 6'362 | 5'153 | 4'291 | 3'654 | 15:85 | 19'48 | 13'85 | 10'30 | |
| 30:70 | 8'935 | 7'408 | 6'102 | 5'110 | 20:80 | 20'73 | 15'36 | 11'69 | |
| 40:60 | 13'33 | 10'95 | 9'111 | 7'691 | 30:70 | 27'45 | 20'88 | 16'20 | |
| | | | | | 40:60 | 38'68 | 29'52 | 22'82 | |
| Conc. of shellac=40%. | | | | | Conc. of shellac=45% | | | | |
| 10:90 | 116'2 | 65'05 | 33'00 | 20'66 | 7'5:92'5 | Gel | Gel | 224'3 | 69'47 |
| 15:85 | 88'35 | 50'09 | 31'09 | 21'91 | 10:90 | „ | 2995'0 | 149'3 | 64'71 |
| 20:80 | 81'09 | 50'63 | 34'45 | 24'48 | 12'5:87'5 | „ | 389'9 | 120'0 | 61'69 |
| 30:70 | 89'10 | 65'26 | 47'41 | 33'26 | 15:85 | 363'2 | 289'2 | 114'6 | 61'48 |
| 40:60 | 126'2 | 89'86 | 65'02 | 47'75 | 20:80 | 487'6 | 209'9 | 112'3 | 67'85 |
| | | | | | 30:70 | 344'2 | 208'6 | 129'6 | 86'10 |
| | | | | | 40:60 | 398'2 | 259'0 | 168'8 | 116'6 |

Shellac in Glycol-Acetone Mixture.

The solvent used is firstly a mixture of glycol and acetone, both of which individually are non-solvents for shellac but the mixture is an excellent solvent from about 5:95 glycol-acetone to a composition of about 90:10. The study of this system has particular advantage over the acetone-water system already studied in that, here a wide range of solvent compositions (5 to 90% glycol) is available for study as against 5 to 25% water in the previous case; hence, a more detailed nature of the viscosity curves is expected to be manifest by a study of this case. Viscosities have been determined for 25, 35, 40 and 45% shellac in mixtures containing various proportions of glycol and acetone at 15°, 20°, 25° and 30°. The results are summarised in Table I and graphically represented in Figs. 1, 2 and 3.

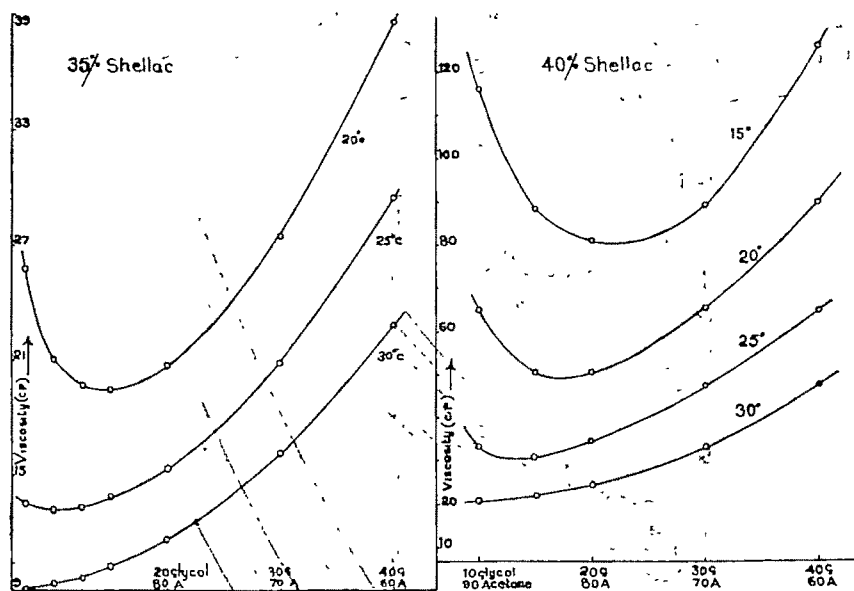
FIG. 1.



Viscosity curves for shellac in glycol-acetone mixture. (Inset, curves for pure solvent mixture).

The viscosity curves for 45% shellac (Fig. 3) all show sharp minima, the position of the minima varying somewhat with temperature. Thus the minimum at 15° is at 27 glycol: 73 acetone, at 20° is at 23 glycol: 77 acetone, at 25° is at 18 glycol: 82 acetone and at 30° at 14 glycol: 86 acetone, showing a gradual drift of the minimum viscosity towards higher concentration of glycol with lower temperature. This is quite a general trend as can also be observed from the positions of the

FIG. 2

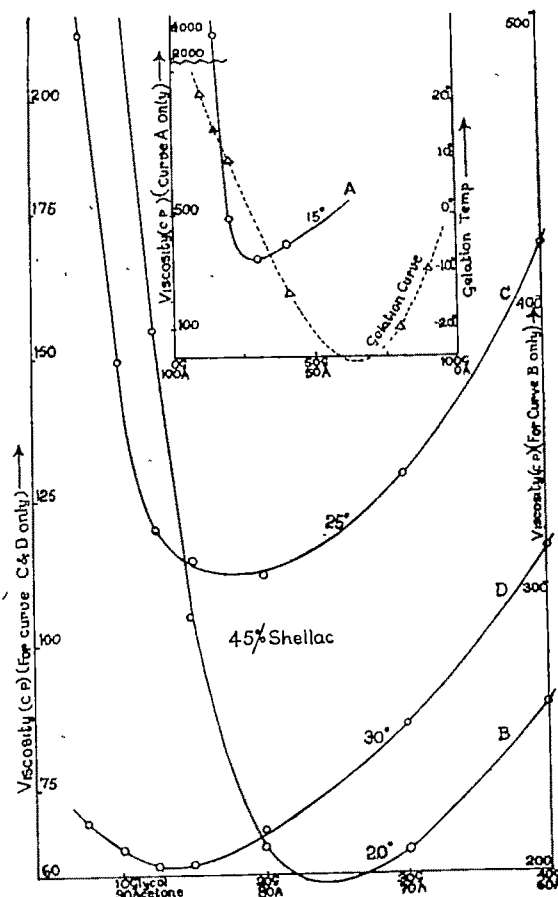


Viscosity curves for shellac in glycol-acetone mixture.

minima for the set of curves for 40% and 35% shellac (Fig. 2). It is further to be noted that the curves are particularly steep towards the acetone side, the steepness rapidly decreasing with rise of temperature. In fact, for 40% and 35% shellac concentrations, the steepness by the pure acetone side flattens so much with rise of temperature, that the minimum vanishes at 30° giving rise to continuously rising curve. The set of curves at 25% shellac concentration (Fig. 1), however, shows no minimum at any of these temperatures but smoothly rises with glycol concentration just like a pure acetone-glycol mixture. It may be further observed that at the same temperature with increasing concentrations of shellac, the viscosity minimum changes towards a higher concentration of the hydroxylic solvent (glycol). For example, at 20° the viscosity

minima are at 17, 19 and 22% of glycol for 35, 40 and 45% concentrations of shellac respectively. The fact that the position of the minimum changes with concentration of the solute and vanishes below some particular concentration of the solute has been first observed in the previous paper, but that it changes appreciably with temperature and may vanish beyond a definite temperature at a particular concentration of shellac is now well established from the data presented herein.

FIG 3.

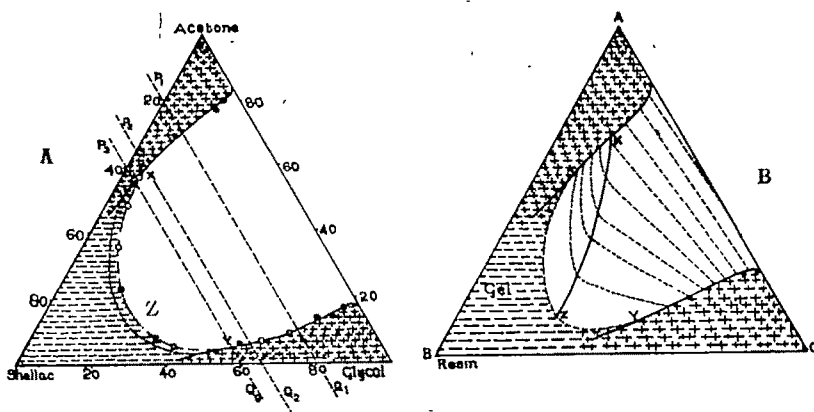


Viscosity curves for 45% shellac in glycol-acetone mixture (curves A, B, C & D); (Inset, gelation curve).

In the previous paper it has been suggested that such viscosity minima exist only above the minimum gelation concentration, i.e., such lowest

concentration of shellac solution as forms gel on cooling instead of separating out in flakes. In an attempt to determine the minimum gelation concentration for such systems, it has been observed that this depends greatly on the composition of the solvent (i.e. proportion of glycol to acetone). A determination of the whole gelation curve is therefore indicated to be necessary to arrive at an understanding of the viscosity curves. The complete solubility and gelation data have therefore been determined at 25° and are graphically represented in Fig. 4A. For the experimental method of obtaining solubility and gelation data for such diagram, a later paper of this series is referred to where an extensive study of such data has been made, which has led to some important and interesting conclusions about the solvent-solute relationship for resins. In the graph (Fig. 4A),

FIG. 4.



A Solubility and gelation curves of shellac in glycol-acetone mixture

B. Constant viscosity diagram of resins in mixed solvents

the crossed portions indicate non-homogeneity whereas the lightly shaded portions (parallel broken lines) are homogeneous transparent gels and the blank portions signify clear solutions.

Referring to our viscosity studies at constant shellac concentration for different compositions of the solvent mixture, this corresponds on the triangular diagram to the viscosity change along a line parallel to the side opposite to the shellac corner. It may be observed that the gelation curve is reached earlier at the acetone-rich end than at the glycol-rich end; for example, the first appearance of gelation occurs at about 34% shellac at the acetone-rich end (X) and at about 43% shellac at the glycol-rich end (Y). Hence, proceeding along a line, such as P_3Q_3 (40% shellac), the viscosity will naturally decrease sharply as the proportion of

glycol increases, since we are thereby passing from a typical gel to a free-flowing solution and then it will slowly increase with increase of concentration of the more viscous component, glycol as usual. This well explains the initial steep fall of the observed curves, and the subsequent comparatively slow rise. As the concentration of shellac further increases, the line P_3Q_3 approaches the gelation line at the glycol-rich end also and ultimately meets it at about 43% shellac. Hence, at 45% shellac concentration, both sides of the curve are observed to be very steep producing a typical U, the acetone-rich arm of which being steeper due to its much stronger gelation capacity. At 35% shellac concentration, the minimum is seen to exist at 25°, but the curve is rather flat. The explanation for this is that the line P_2Q_2 for 35% shellac just fails to pass through the gelation range, hence the initial high value is due to incipient gelation which evidently cannot produce a steepness in viscosity curve equal to that of actual gelation. It is thus evident why with decrease in concentration of shellac, the minimum shifts towards lower concentration of glycol and at about 35% shellac, the minimum is practically adjacent to the insolubility region. On further lowering of shellac concentration, the minimum merges into the insoluble region and hence the actual curves show no minima. This really happens for 25% and less of shellac, where the experimental curves are smooth continuously rising ones (Fig. 1).

The fact that at constant temperature with increase of shellac concentration, the minimum in the viscosity curve drifts towards higher concentration of glycol, is thus ascribed to a lack of symmetry of the course of the gelation curve. It may hence be safely inferred that the drift of the the minimum viscosity towards higher glycol concentration will certainly continue with increase in concentration of shellac and will ultimately approach and, in the limiting case, coincide with a composition corresponding to the point, Z, where the gelation curve XZY just touches a parallel line to AC (Fig. 4B).

The already mentioned effect of temperature on the viscosity minimum can also be explained from the three-component diagram. With increase of temperature the gelation curve naturally recedes towards higher concentration of shellac but the point X has been experimentally observed to recede along AX at a more rapid rate than Y along CY, i.e. generally speaking the gelation temperature changes more rapidly with concentration of shellac, as the solvent mixture gets richer in the hydroxylic component. The approximate gelation line at 30° has also been shown in Fig. 4A as a broken line, somewhat parallel to XZY; of course, the position of the line AX and CY will change to some extent but this has

not been shown in the figure. Hence, with rise of temperature any line, PQ, will tend to cut less gelation area in the acetone rich side than at the glycol-rich side as a result of which the minimum will tend to get shifted towards a lower concentration of glycol by such rise of temperature. The shift of minimum towards lower concentration of glycol at higher temperature may be so great as to displace it in the insolubility region. The experimental curves will then have no minima and this really happens at 30° for 35% and 40% shellac concentrations where the corresponding curves may be seen to have no minima (Fig. 2).

A very striking fact about the effect of temperature on the viscosity of such lyophilic solutions should be pointed out. From even a casual examination of the graphs, it is apparent that the temperature coefficient of viscosity is higher at the two extremes than at near about the minimum viscosity compositions. In other words, for equal lowering of temperature, the viscosity increases much less at near about the minimum viscosity than at other points. There is, however, no definite composition at which the temperature coefficient of viscosity is least, since this depends to some extent on the temperature as well as on the concentration of the resin.

It is thus clear that the viscosity behaviour of such systems is determined by their solubility and gelation capacity and the once widely upheld idea of an optimum composition of solvent mixture producing solution of lowest viscosity is proved to be inadequate. In a restricted sense, however, the solvent composition corresponding to the point Z, the apex of the gelation curve, may be termed as an optimum solvent mixture. It is to be noted in this connection that though the minimum in the viscosity curves in the temperature and concentration studied generally lie within the limits, 10 glycol : 90 acetone to 30 glycol : 70 acetone, the gelation curve (Fig. 3, inset) shows no minimum in this range but its minimum lies at about 64 glycol : 36 acetone—a solvent composition approximately equal to that of the point Z. This trend of the minimum in the gelation curves to be richer in the more polar component has already been observed in our previous work with acetone-water, but for reasons already stated, the difference is not so prominently perceptible there as to merit a confident mention. This is, however, of real moment and shows the importance of the point Z, as containing the optimum solvent composition at the corresponding temperature. This fact is also true for shellac-glycol methyl acetate and shellac-acetone-alcohol systems and other systems to be referred to later where the viscosity minima always lie wide apart from the gelation minimum and at a much lower proportion of the hydroxylic component.

Shellac in Glycol-Methyl Acetate Mixture.

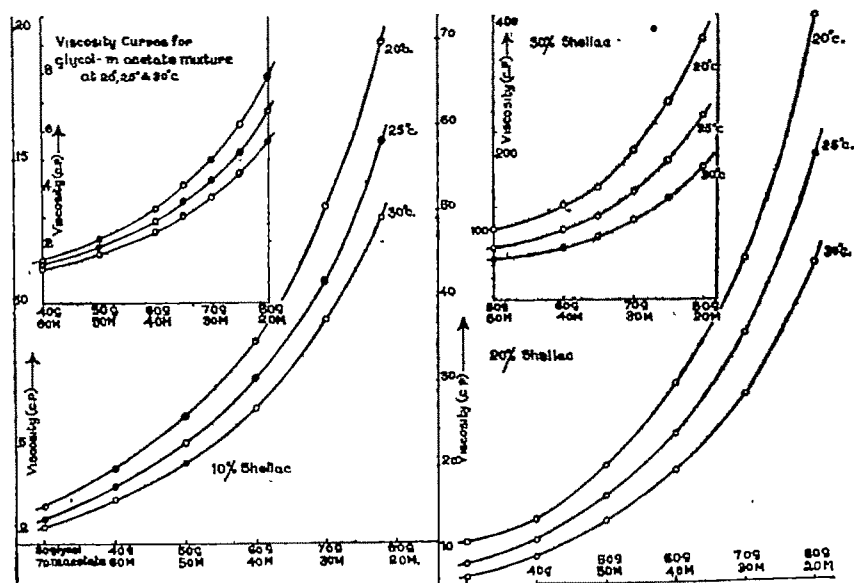
A mixture of glycol and methyl acetate both of which are individually non-solvents for shellac, has also been studied with reference to the above behaviour. The mixture has good solvent power for shellac from a composition of about 30 to 80% glycol. Viscosity studies have been made with 10, 20, 30, 35, 45 and 50% of shellac solutions in different compositions of this solvent mixture at 30°, 25° and 20°, and a few also at 15°. The results are given in Table II and are graphically represented in Figs. 5, 6 and 7.

TABLE II.

| Solvent by wt.) Glycol· methyl acetate. | Viscosity (centipoise) at | | | | Solvent (by wt.) Glycol· methyl acetate. | Viscosity (centipoise) at | | | |
|---|---------------------------|--------|--------|--------|--|---------------------------|-------|-------|-------|
| | 15° | 20° | 25° | 30° | | 15° | 20° | 25° | 30° |
| Conc. of shellac=10%. | | | | | Conc. of shellac=20%. | | | | |
| 30:70 | | 2'87 | 2'39 | 2'10 | 30:70 | | 10'98 | 8'48 | 6'876 |
| 40:60 | | 4'17 | 3'54 | 3'07 | 40:60 | | 13'55 | 11'08 | 9'226 |
| 50:50 | | 6'00 | 5'06 | 4'36 | 50:50 | | 19'99 | 16'25 | 13'35 |
| 60:40 | | 8'65 | 7'35 | 6'28 | 60:40 | | 29'49 | 23'64 | 19'25 |
| 70:30 | | 13'35 | 10'77 | 9'38 | 70:30 | | 44'27 | 35'50 | 28'33 |
| 80:20 | | 19'14 | 15'65 | 12'99 | 80:20 | | 72'71 | 56'41 | 43'90 |
| Conc. of shellac=30%. | | | | | Conc. of shellac=35%. | | | | |
| 50:50 | | 100'2 | 74'82 | 57'19 | 30:70 | | 136'2 | 90'86 | 64'45 |
| 60:40 | | 133'3 | 99'86 | 75'09 | 40:60 | | 190'1 | 127'8 | 89'78 |
| 65:35 | | 159'9 | 118'0 | 88'84 | 50:50 | | 251'6 | 171'6 | 121'6 |
| 70:30 | | 210'8 | 152'9 | 112'9 | 60:40 | | 353'0 | 246'7 | 177'9 |
| 75:25 | | 278'1 | 196'2 | 143'0 | 65:35 | | 474'7 | 327'7 | 229'2 |
| 80:20 | | 365'5 | 259'5 | 186'8 | 70:30 | | 606'2 | 416'9 | 288'7 |
| | | | | | 80:20 | | 974'7 | 651'3 | 447'2 |
| Conc. of shellac=45%. | | | | | Conc. of shellac=50%. | | | | |
| 30:70 | 1276'0 | 633'9 | 365'9 | 227'0 | 30:70 | 81'300 | 4439 | 1538 | 714'8 |
| 40:60 | 986'5 | 601'6 | 379'6 | 251'5 | 40:60 | 5'323 | 2'382 | 1234 | 697'7 |
| 50:50 | 1063'0 | 676'1 | 444'5 | 309'3 | 50:50 | 5256 | 2787 | 1555 | 915'2 |
| 60:40 | 1505'0 | 966'2 | 634'8 | 425'1 | 60:40 | 6785 | 3776 | 2185 | 1313 |
| 70:30 | 2330'0 | 1477'0 | 968'5 | 640'0 | 80:20 | 15'980 | 9313 | 5520 | 3232 |
| 80:20 | 3967'0 | 2460'0 | 1569'0 | 1028'0 | | | | | |

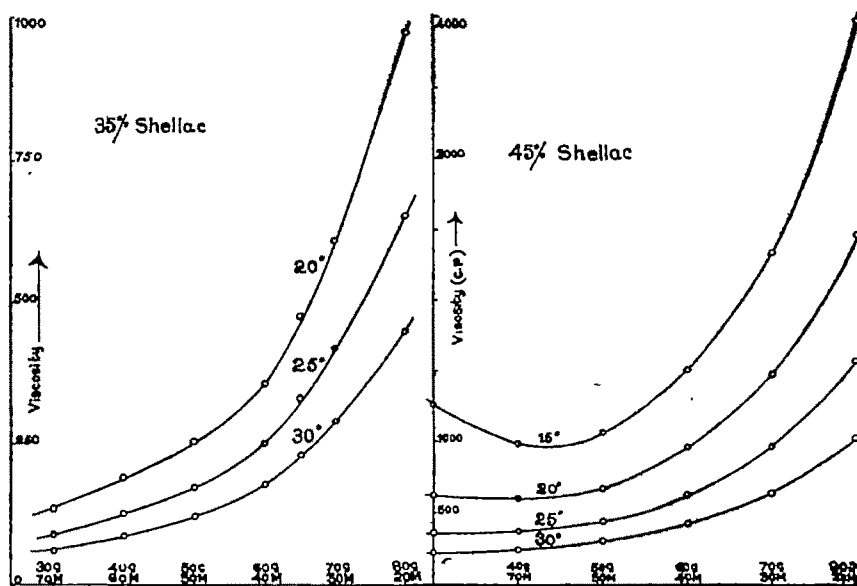
All the curves up to 35% shellac concentration (Fig. 5 and 6) show a continuous rise of viscosity with increase in the proportion of the

FIG. 5.



Viscosity curves for shellac in glycol-acetone mixture

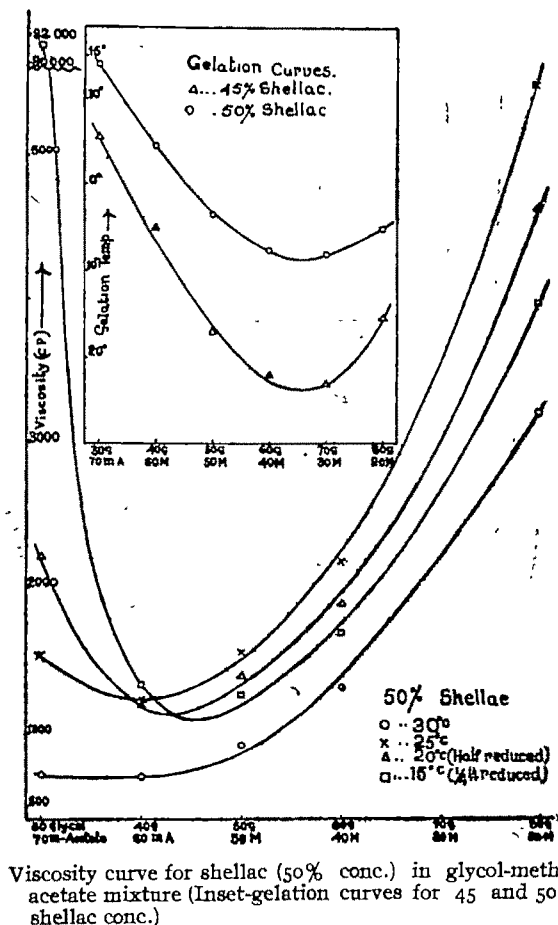
FIG. 6.



Viscosity curves for shellac in glycol-methyl acetate mixture.

more viscous component, glycol, just like pure glycol-methyl acetate mixture. The first appearance of minimum in the viscosity curve occurs at 45% shellac concentration at 20°, rather distinctly at 15° (Fig. 6). At 50% shellac concentration, the minima are all very well-marked (Fig. 7). The relative change of position of the minima with variation of temperature and concentration of shellac is similar to that noticed in the previous case of glycol-acetone and is likewise very distinctly observable here. There are also other points of resemblance which we omit to refer to as a side comparison of the different graphs easily brings them to light.

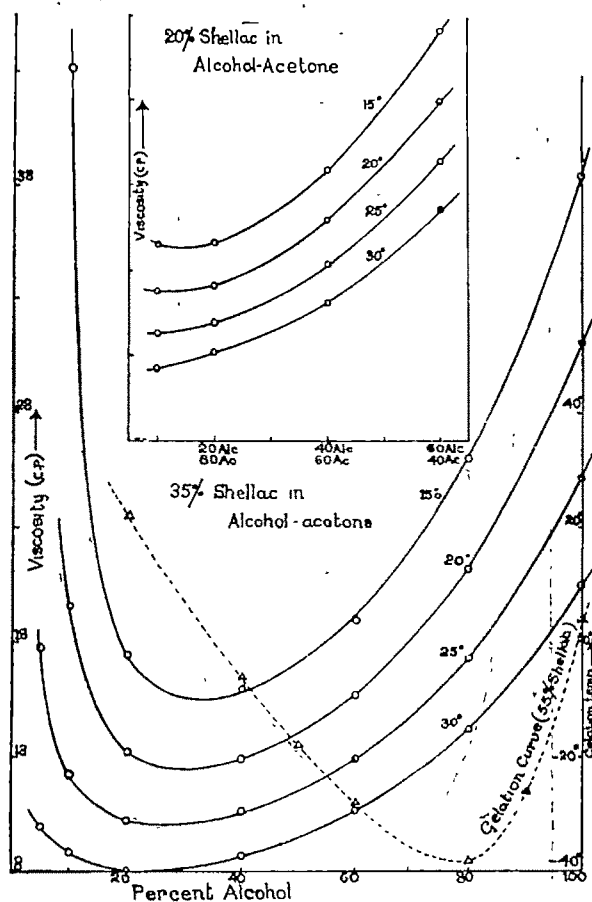
FIG. 7.



It is further to be noted that though the viscosity minima lie at about 40 to 50% glycol, the gelation curves show minima at 66% glycol, which, however, lie at about the same value for 45 and 50%

concentrations of shellac. The precipitation curves for lower concentrations of shellac (experimentally determined for 10% and 20% shellac) also tend to show minima at about the same solvent composition, but the curves are not so smooth since the phase which separates at the precipitation temperature is in some cases liquid and in some cases solvated solid.

FIG. 8.



Viscosity curve for shellac (35% conc.) in acetone-alcohol mixture (Inset for 20% conc. of shellac). Dotted curve represents gelation curve for 55% shellac conc.).

Shellac in Alcohol-Acetone Mixture.

These general considerations appear to be applicable even with a solvent-latent solvent mixture, and mixtures of alcohol and acetone have been studied to test this point. Measurements of viscosity have been made at

25 and 35% shellac concentrations in various compositions of the solvent mixture at 15°, 20°, 25° and 30°. The results are presented in Table III and graphically represented in Fig. 8.

TABLE III.

| Solvent (by wt.). Alcohol: acetone | Viscosity (centipoise) at | | | | Solvent (by wt.). Alcohol: acetone | Viscosity (centipoise) at | | | |
|---|---------------------------|-------|-------|-------|---|---------------------------|-------|-------|-------|
| | 15° | 20° | 25° | 30°. | | 15°. | 20°. | 25° | 30°. |
| | Conc. of shellac = 20% | | | | | Conc. of shellac = 35%. | | | |
| 10:90 | 2.023 | 1.765 | 1.541 | 1.353 | 5:95 | Gel | Gel | 17.75 | 9.978 |
| 20:80 | 2.024 | 1.799 | 1.603 | 1.443 | 10:90 | 43.11 | 19.61 | 12.34 | 8.851 |
| 40:60 | 2.427 | 2.154 | 1.928 | 1.722 | 20:80 | 17.41 | 13.20 | 10.19 | 8.050 |
| 60:40 | 3.206 | 2.823 | 2.496 | 2.245 | 60:40 | 18.98 | 15.58 | 12.86 | 10.66 |
| | | | | | 80:20 | 26.01 | 21.31 | 17.34 | 14.28 |
| | | | | | 100:0 | 38.40 | 31.10 | 25.24 | 20.50 |

The gelation or precipitation temperature could not be measured at these shellac concentrations as some of them are inconveniently low (below 60%) and hence the gelation temperatures at 55% shellac concentrations have been plotted as dotted curve in the figure. All the features of the foregoing curves with respect to the effect of temperature and concentration are also manifest here. Thus the curves for 35% shellac all show minima at between 20 and 32% alcohol. The curves at 25° and 30° at 20% concentration of shellac show no minima but are continuously rising ones like that of the pure solvent mixture, whereas the curves for lower temperatures (15° and 20°) tend to show minima at very low concentrations (about 15%) of alcohol. The fact that viscosity minimum drifts towards a lower concentration of the hydroxylic solvent with rising temperature tending to vanish above a certain temperature, is thus too apparent. It may be further pointed out as a basic cause of the viscosity minimum lying in the acetone-rich end, that here also the gelation curve is unsymmetrical, gelation being more favoured at the acetone-rich end than at the alcoholic end. The complete curve has been experimentally determined and will appear at the more appropriate place in a later paper dealing with solvent-solute relationship in resins.

As already pointed out in the previous cases, the viscosity minimum is also here widely separated from the gelation minimum, which is at about 80% alcohol. Since this composition, which gives the minimum

gelation temperature, approximates to that of the point Z (in the three component diagram), we shall henceforth term this composition as the optimum solvent mixture, as the composition of the point Z is not so accurately determinable. This gelation minimum is adopted as the optimum composition instead of the point Z, which is the true optimum solvent composition for experimental convenience only; nevertheless, the point Z, is of fundamental significance. Hence, the true optimum solvent composition may be given the following formal definition. The optimum solvent composition is that mixture which requires the highest concentration of the lyophilic solute at any given temperature to just produce gelation.

One pertinent fact about this optimum composition may now be mentioned. For a mixture containing a good solvent (alcohol) and a semi-solvent (acetone), the optimum composition contains a preponderance of the former. If this is assumed as a basic truth, the determination of optimum composition by this method gives us a rational method of assessing the solvent power for lyophilic solutes, for then we have simply to determine the optimum composition for a mixture of two solvents by this procedure. That quite reasonable values are obtainable by such methods is evident from the calculated values of solvent power for the following solvents for shellac (*vide* Table IV). The second column gives the observed optimum solvent compositions for pairs of solvents, and the fourth column contains calculated values of solvent power for the individual solvents assuming that the optimum solvent composition denotes the ratio of the solvent power of the component solvents. The physical significance of solvent power for non-solvents lies perhaps, in its power of solvation of the lyophilic units present in solution. The proper test, however, of such a method is its ability to yield the same value of the solvent power ratio of two latent solvents by comparison with two different third solvents.

TABLE IV.

| Solvent mixture. | Optimum solvent comp | Solvents. | Solvent power. (Alcohol=100). |
|-------------------------|----------------------|----------------|-------------------------------|
| Water : acetone | 14 : 86 | Alcohol | 100 |
| Glycol : acetone | 64 : 36 | Glycol | 44 |
| Glycol : methyl acetate | 70 : 30 | Acetone | 25 |
| Alcohol : acetone | 80 : 20 | Methyl acetate | 19 |
| | | Water | 4 |

DISCUSSION.

Perhaps, the optimum solvent compositions with different solvent mixtures may furnish some important indications of the structure of the shellac molecule but due to the unsatisfactory state of our knowledge of molecular adsorption forces and polarity, no definite information is available. The idea of an optimum polarity is of no help as calculations of dipole moments of these mixtures on the assumption of additivity of dipole moments do not yield even nearly uniform values.

It is of great interest and usefulness to draw lines of equal viscosity on such three-component diagrams. Instead of constructing it for any particular case, the general courses of such lines in a typical case have been indicated in the figure (Fig. 4B) as dotted lines. This figure is based on the above-mentioned experimentally observed facts that proceeding along any line towards B (*i.e.* increasing shellac concentration) the viscosity increases almost logarithmically with concentration. But proceeding along a line, parallel to AC, viscosity rises steadily but much less rapidly with increase in proportion of the hydroxylic solvent C up to a certain concentration of shellac and then it shows minima. The thick line is obtained by joining the points of minimum viscosity and it cuts the solubility line at the point K. So, all concentrations, less than this value, do not show minimum viscosity, while above it viscosity curves will have minima. Any line of constant viscosity, which passes below the point K, is continuously increasing its ordinate on the line AC (signifying increase of shellac concentration) as it proceeds from the C-corner to the B-corner. Lines passing above the point K, *i.e.*, cutting the line ZK should, however, necessarily have maxima with respect to the line AC. The curves are self-explanatory and such diagrams should yield the technically very important information of how the viscosity of a varnish varies by dilution with the component solvents.

Such curves are presumably also valid for pyroxylin solutions, with the difference that the points K and X occur at a much lower concentration of nitrocellulose. The constant viscosity method developed during the last few years (Doolittle, *Ind. Eng. Chem.*, 1938, 30, 189; Ware and Teeters, *ibid.*, 1939, 31, 738) which proposes to find out that composition of the solvent mixture, which has the maximum solid content for a given viscosity, evidently yields any point on the line ZK instead of the true optimum composition, Z, the position of this so-called optimum solvent ratio, hence depending on the viscosity chosen for comparison. Doolittle's phase diagram, however, affords data useful to lacquer industry and is certainly

to be regarded as the first rational attempt towards solvent power evaluation. One point about Doolittle's phase diagram, however, is not clear to the author. It is a mathematical truth that in any smooth parabolic type curve, such as the viscosity curves of ours as well as of Doolittle, the point of maximum curvature is certainly the minimum point in the curve, whereas Doolittle has drawn (*vide* his Fig. 19) two straight lines supposed to pass through these minimum curvature points. By doing so, the two lines will meet at a point (*vide* his Fig. 20), which according to him is the optimum composition. Evidently, this point again is not our true optimum composition Z , but is a composition of the line KZ , which is nearest possible to Z with the maximum workable viscosity. In a later paper of this series, now under publication, the author has attempted to present a generalised picture of such viscosity changes, which may help to clarify the situation.

It is now clear that the explanation of viscosity of a resin solution has its root in the gelation capacity of the system and such solutions above the minimum gelation concentration may be regarded in a limited sense as incipient gels. This shows the importance of gelation studies of such systems, work on which are under progress and will constitute a later publication.

We may now summarise the facts we have been able to establish about solutions of shellac in a mixture of two non-solvents. Three types of viscosity curves are possible as described below under (a), (b) and (c) and the effects of temperature and concentration are shortly summarised under (d) and (e) below:—

Type (a).—The viscosity curve is somewhat steeper than that of the pure solvent mixture and shows no minimum, but a continuous increase of viscosity with increase in proportion of the hydroxylic solvent. This generally happens for low concentrations of shellac, which is far off the minimum gelation concentration.

Type (b).—The viscosity curve is characterised by a steep fall followed by a slow rise, somewhat steeper than that of the pure solvent mixture. This tends to take place nearing that concentration of shellac which produces gelation at only one extreme of the solvent compositions.

Type (c).—The viscosity curve is very steep on both sides and so assumes almost a U-shape. This occurs when the concentration of shellac is such as to produce gelation at both extremes of the solvent compositions.

(d) *Effect of Temperature.*—The effect of higher temperature is to displace the minimum to a lower concentration of the hydroxylic solvent

and to tend to flatten the arms of the **U** of the viscosity curves. If the temperature is sufficiently high, the minima will vanish from the experimental curve and the viscosity curves will be of type (a) above.

(e) *Effect of Concentration*.—With increase of concentration of shellac, the minimum steadily shifts to a higher proportion of the hydroxylic solvent, *i.e.* towards the so-called optimum solvent composition. The arms of the viscosity curves also become steeper.

Before attempting an explanation of the different types of viscosity curves we must first acknowledge the limitations of the existing theoretical developments on viscosity of lyophilic solutions. Recently a number of attempts have been made to modify Einstein's equation for viscosity of a colloidal dispersion to quantitatively include cases of lyophilic solutions with unsymmetrical particles, a resumé of which appears in a recent book (H. Mark, "High Polymers," 1940, **II**, 294). A very complete and systematic account of the present trend of these theoretical researches on viscosity of liquids, solutions and high polymers can be obtained from three reviews by Barr, Goodeve and Eirich respectively ("Annual Reports on the Progress of Physics", 1936, **3**, 19; 1938, **5**, 20; 1940, **7**, 329); and also in Reports on Viscosity and Plasticity, specially papers by Bungenberg de Jong, First Report, 1939, 2nd Ed, Ch. III, p. 110; Burgers, Second Report, 1938, Ch. I, p. 1, and Jaeger, *ibid.*, 1938, Ch. II, p. 29). These researches seem to have received stimulus from Staudinger's work on viscosity of high molecular weight solutes but they are still in the course of development and so cannot be profitably invoked to our aid. Though no body denies the important role which solvation plays in such solutions, there is yet no reliable, even approximate, method of knowing the extent of solvation and its influence on other properties, such as viscosity, surface tension, etc. of the solution.

For a qualitative picture we may imagine that due to high solvation, a good portion of the solvent gets immobilised resulting in higher viscosity and hence the viscosity curves are of the same shape as that of the pure solvent mixture ('a' curves). How a typical gel of almost infinite viscosity is broken down to a fluid of viscosity of even less than a poise with increase in proportion of one of the solvents is difficult to explain. If gelation is assumed to be due to mutual coalescence of the 'solvation layer' made of hydroxylic solvent, due to their characteristic association tendency the explanation is apparent. A higher proportion of hydroxylic solvent stops this mutual coalescence between the neighbouring 'solvation layers' and so brings about a lowering of viscosity. However, any such theoretical idea

must be highly tentative and so it is evidently of no use to make a detailed examination of the data in this light. But these data in conjunction with the modern developments on lyophilic solutes, particularly high polymers, are able to present a fairly complete and connected qualitative picture of the whole field, which we shall attempt to do in the next part of this investigation, where the results of further similar studies for other lyophilic solutes, like other resins, cellulose derivatives, etc. will be presented.

The author acknowledges with great pleasure the help and encouragement he has received from Dr. H. K. Sen, Director, Indian Lac Research Institute, throughout the course of this investigation.

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APPLICATION OF HAMMICK AND ANDREW'S FORMULAE FOR DETERMINING THE PARACHOR OF A SOLUTE.

BY W. V. BHAGWAT AND P. M. TOSHNIWAL.

It is shown that Hammick and Andrew's equation for the parachor of a solute holds under all conditions, *i.e.*, when (a) number of molecules in solution remains equal to the sum of the molecules of the constituents, (b) when they are equal to the solvent molecules only, (c) when they remain equal to solute molecules only, or (d) when there is ionisation. Lakhani and Daroga's modification is proved to be incorrect. In case of salts it is assumed that ionic and atomic parachors are identical. It is further shown that parachor of an associated solute is n times the parachor of simple molecules

Hammick and Andrew's formula (*J. Chem. Soc.*, 1929, 754)

$$P_{\text{M}} = (1-x)P_{\text{P}} + xP_{\text{S}}$$

where P_{M} is the observed parachor of the solution containing a fraction of solute molecules, P_{P} = the parachor of the solvent and P_{S} , the parachor of the solute. The equation has been verified in case of several liquids and solids.

Lakhani and Daroga (*J. Indian Chem. Soc.*, 1938, **15**, 37, 520) have tried to extend this work to inorganic salts and have advocated a modification of the above formulae on the ground, that when liquids are mixed, the volume is in general equal to the sum of the volumes of the constituents but when a solid is dissolved, the volume change is negligible. Therefore, since according to Sudgen's equation

$$P = V\gamma^{\frac{1}{4}}$$

where V is the molecular volume or as in Hammick and Andrew's equation

$$P_{\text{M}} = V_{\text{M}}\gamma^{\frac{1}{4}}$$

where V_{M} is the mean molecular volume, the parachor values calculated by the above equation, when inorganic salts are dissolved in the solvent, will be half as when liquids are dissolved. Consequently Hammick and Andrew's equation when applied to the inorganic solutes in solution and when volume changes are negligible should be written as

$$P_{\text{M}} = (1-x)P_{\text{P}} + x\frac{P_{\text{S}}}{2}.$$

These authors have verified this equation in the case of numerous inorganic salts.

The modification introduced by Lakhani and Daroga is, however, open to objection since

(a) The mean molecular weight has nothing to do with volume of the system, but is solely determined by the total weight and total number of molecules.

(b) It is not necessary that for all values of x , the molecular weight calculated according to their suggestion should become double the value obtained by Hammick and Andrew's equation

$$M_M = (1-x)M_r + xM_s$$

where M_M = mean molecular weight, M_r = the molecular weight of the solvent and M_s = the molecular weight of the solute.

(c) As it will be shown below the equation of Hammick and Andrew's remains unchanged whether we assume (i) that total number of molecules after mixing = the sum of the molecules of the constituents, (ii) equal to the number of solvent molecules, and (iii) equal to the number of solute molecules.

(d) The equation also remains unchanged even if we assume that salts ionise, provided ionic and atomic parachors are identified.

Moreover, it appears that they have not verified their equation with actual results. They have substituted a value of 54 for the parachor of water (*J. Chem. Soc.*, 1924, **125**, 1188), which is apparently too high and cannot be justified since the value given by Sudgen is 52.3 ("Parachor", 1930; *vide* also International Critical Table, 1929, **IV**, 447). They have not found out the value of P_r for themselves. The value for P_r for water as obtained by Ray (*J. Indian Chem. Soc.*, 1938, **15**, 43) is 52.6. It is clear therefore that to verify their equation, value of P_s should be taken to be 52.3. With this value, we are afraid, their equation completely breaks down as the following table shows.

TABLE I.

| Salts. | x . | P_M . | P_M with $P_r = 52.3$. | P_M calc. |
|------------------|--------|---------|---------------------------|-------------|
| KCl | 0.0588 | 53.56 | 215.2 | 162.7 |
| KBr | 0.0434 | 55.49 | 255.2 | 176.4 |
| KI | 0.0368 | 55.67 | 288.6 | 199.4 |
| KNO ₃ | 0.0426 | 55.98 | 276.8 | 200.9 |

We have recalculated all their results (*J. Indian Chem. Soc.*, 1938, **15**, 43) and have observed that the equation completely breaks down.

In case of KClO₃, KBrO₃ and KClO₄ even with $P_r = 54$ the values become absurd (Table II).

TABLE II.

| Salt. | α . | P_M . | P_x with $P_P=54$ by Lakhani. | P_x with $P=54$ by Authors. |
|-------------------|------------|---------|------------------------------------|----------------------------------|
| KClO ₃ | 0.0216 | 53.4 | 218 | 52.7 |
| KBrO ₃ | 0.0159 | 53.19 | 231.2 | 7.5 |
| KClO ₄ | 0.0103 | 52.86 | 237.2 | —ve |

Strangely enough in case of NaNO₃ (*ibid.*, 1938, 15, 520) they have used Hammick and Andrew's equation instead of their own.

They have suggested that in Ray's results (*J. Indian Chem. Soc.*, 1938, 15, 43) the observed parachor of ammonium salts approach the calculated value if their equation is employed. But in reality the results so obtained appear to be different as compared to the calculated values.

TABLE III.

NH₄Cl in H₂O.

| α . | P_M . | P_x with $P_P=54$ Lakhani's equation. | P_x calc. |
|------------|---------|--|-------------|
| 0.00662 | 52.7 | Negative | 133.6 |
| 0.00977 | 52.97 | " | 133.6 |
| 0.0111 | 53.28 | " | 133.6 |
| 0.07614 | 57.79 | 210 | 133.6 |
| 0.09915 | 59.40 | 217 | 133.6 |

Hammick and Andrew have derived their equation on the assumption that the total number of molecules in solution remains equal to the sum of the molecules of the constituents. This need not be so. The number of molecules in solution may be equal to that of solute or solvent or may change due to association or dissociation of solute molecules. We shall now consider how far the equation of Hammick and Andrew holds even in these cases.

The Total Molecules in Solution = the Molecules of Solvent.

In this case the solute molecules may be said to distribute themselves equally amongst all the solvent molecules to form new molecules, thus keeping the molecules in solution equal in number to solvent molecules. Hence

if x represents the number of solute molecules distributed per solvent molecule, the weight of the new molecule = weight of one molecule of solvent + weight of x_1 molecules of solute

$$\text{or} \quad M'_x = M_p + x_1 M_x \quad \dots (i)$$

where M'_x = the molecular weight of the new molecules.

In Hammick and Andrew's equation, λ represents the number of molecules of solute per $(1-\lambda)$ molecules of solvent. Hence the number of molecules of solute per molecule of solvent = x_1 is given by the relation

$$\lambda_1 = \frac{x}{1-x} \quad \dots (ii)$$

Substituting this value we get

$$M'_x = M_p + \frac{x}{1-x} M_x \quad \dots (iii)$$

$$\text{or} \quad (1-x)M'_x = (1-x)M_p + xM_x$$

But by Hammick's equation

$$M_x = (1-x)M_p + xM_x$$

$$\text{Hence} \quad (1-x)M'_x = M_x \quad \dots (iv)$$

The value of parachor of the solute P'_x for the new molecule will be given by

$$P'_x = \frac{M'_x}{d} \gamma^{\frac{1}{4}}$$

$$\text{Substituting the value of } M'_x = \frac{M_x}{1-x},$$

$$\text{we get} \quad P'_x = \frac{M_x}{d(1-x)} \gamma^{\frac{1}{4}}$$

$$\text{But} \quad P_x = \frac{M_x}{d} \gamma^{\frac{1}{4}}$$

$$\text{Hence} \quad P'_x = \frac{P_x}{1-x}$$

This value will be $= 2P_x$ if $x = \frac{1}{2}$; and not for all values of x as suggested by Lakhani and Daroga. The parachor of the new molecule is given by the equation

$$P'_x = P_p + x_1 P_x$$

if parachor is an additive property and therefore equal to parachor of one molecule of solvent + x molecules of solute. Substituting the values of P'_x and x_1 we get

$$\frac{P_x}{1-x} = P_p + \frac{x}{1-x} P_x$$

or

$$P_x = (1-x)P_p + xP_x.$$

Thus the equation of Hammick and Andrew remains unchanged and hence gives the correct values of P'_x . In a similar way it can be shown without difficulty that Hammick and Andrew's equation holds good *when the total molecules = molecules of solute, and also when solute ionises.*

The nature of the expression when solute molecules undergo association is discussed below.

When Solute Molecules Associate.

Let us now suppose that solute associates, so that n molecules form one molecule.

$$nA = (A)_n.$$

If x be the fraction of the number of these associated molecules then mean molecular weight

$$M'_x = (1-x_1)M_p + x_2 M'_n,$$

where M'_x is the molecular weight of the associated molecule of the solute. Hence $M'_x = nM_x$.

If the original fractions of the solvent molecule to solute molecules without polymerisation are as $1-x : x$ then there are $\frac{x}{1-x}$ molecules of solute per molecule of solvent. Hence the number of associated molecules formed is $\frac{x}{n(1-x)}$. Thus the fraction of the associated molecule

$$x_1 = \frac{x/n(1-x)}{1 + \frac{x}{n(1-x)}}$$

or

$$x_1 = \frac{x}{n - (n-1)x}$$

Substituting this value we get

$$\begin{aligned} M'_x &= \left\{ \frac{n(1-x)}{n-(n-1)x} \right\} M_p + \frac{x}{n-(n-1)x} M'_x \\ &= \frac{n}{n-(n-1)x} \{ (1-x)M_p + xM_x \} \\ &= \frac{n}{n-(n-1)x} M_x. \end{aligned}$$

$$\text{Also } P'_x = \frac{M'_x}{d} \cdot \gamma^{\frac{1}{3}} = \frac{nM_x}{n-(n-1)x} \cdot \frac{\gamma^{\frac{1}{3}}}{d} = \frac{nP_x}{n-(n-1)x}.$$

$$\text{But } P'_x = (1-x_2)P_p + x_2P'_x$$

$$\text{or } \frac{P_x \cdot n}{n-(n-1)x} = \frac{n(1-x)}{n-(n-1)x} P_p + \frac{x}{n-(n-1)x} P'_x$$

where P'_x is the parachor of the associated molecule

$$\text{or } nP_x = n(1-x)P_p + xP'_x$$

$$\begin{aligned} \text{or } xP'_x &= nxP_x \quad \text{but this is} \\ &= n\{P_x - (1-x)P_p\} \end{aligned}$$

$$\text{or } P'_x = nP_x.$$

Parachor of associated molecule, provided it is additive, is n times the parachor of a simple molecule. This means it is impossible to detect association of solute by parachor, since in mean molecular weight the value to be substituted for M is n times M . The failure of Hammick and Andrew's formulae therefore must be attributed to some other cause than mentioned above.

CHEMISTRY DEPARTMENT,
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QUANTITATIVE SEPARATION OF CALCIUM FROM STRONTIUM USING ACETONE AS A SOLVENT.

By M. M. TILLU AND M. S. TELANG.

A quantitative separation of calcium from strontium has been effected by using acetone as a solvent. The method is based upon the principle that calcium nitrate is highly soluble in acetone while strontium nitrate is insoluble in the same solvent.

Data on the separation of calcium from strontium in analysis appear to be meagre. One method is to separate the nitrates by a mixture of ether and anhydrous absolute alcohol (1 : 1) ; alternatively, anhydrous amyl alcohol is used (Scott, "Standard Methods of Quantitative Analysis", 1937, Vol I, p. 6). Tananaev reports (*Z. anal. Chem.*, 1935, **100**, 391) the use of glacial acetic acid for their separation as dry nitrates. Further quantitative results confirming this claim are, however, lacking.

With a view to selecting a solvent which is easily accessible in the purest condition, we carried out a series of investigations with various organic solvents and we have found that acetone serves the above purpose quite satisfactorily.

Strontium nitrate is insoluble in acetone while calcium nitrate is highly soluble. It follows, therefore, that the two elements should be present in the mixture as dry nitrates. If they are not initially present as nitrates, they have to be converted into dry nitrates by the usual method (*cf.* Scott, *loc. cit.*).

EXPERIMENTAL.

The order of solubility of strontium nitrate in acetone as found by us at 35° is 1 part in 15,000 parts of acetone. Calcium nitrate is highly soluble.

Various mixtures of calcium nitrate and strontium nitrate were prepared in water solution and the results of analysis according to this procedure have been recorded in the accompanying table.

A known quantity of strontium nitrate solution (about 5%) was taken in a weighing bottle and evaporated to dryness, the weight of the residue corresponding to the amount of strontium nitrate taken. To this residue of strontium nitrate again a known quantity of calcium nitrate solution (about 5%) was added and evaporated to dryness at 170°. The weight

of this residue less the weight of strontium nitrate taken gives the weight of calcium nitrate taken.

The mixture of the dry nitrates was prepared by evaporation and dried at 170° . Calcium nitrate was extracted with acetone from strontium nitrate and the filtration was done through a sintered glass crucible. The acetone solution was evaporated to dryness and the residual calcium nitrate was further dried at 170° and weighed as such. The strontium nitrate left behind after extraction in the sintered glass crucible was dried and weighed.

TABLE I.

| Mixture No | Sr(NO ₃) ₂ | | Ca(NO ₃) ₂ | |
|------------|-----------------------------------|--------|-----------------------------------|--------|
| | Actual | Found | Actual. | Found |
| I | 0.1610 | 0.1594 | 0.1640 | 0.1670 |
| II | 0.1396 | 0.1360 | 0.3880 | 0.3840 |
| III | 0.3430 | 0.3464 | 0.1784 | 0.1740 |
| IV | 0.3240 | 0.3230 | 0.2550 | 0.2542 |
| V | 0.4820 | 0.4800 | 0.1800 | 0.1780 |
| VI | 0.4860 | 0.4854 | 0.3490 | 0.3480 |
| VII | 0.6116 | 0.6120 | 0.1750 | 0.1764 |
| VIII | 0.1600 | 0.1610 | 0.5060 | 0.5070 |
| IX | 0.3184 | 0.3180 | 0.5390 | 0.5400 |

We thank Professor B. V. Mohil  for giving us the necessary facilities and encouragement.

DEPARTMENT OF CHEMISTRY,
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THE ALKALOID OF *BERBERIS UMBELLATA*, WALL. PART II.

BY R. CHATTERJEE.

Umbellatine is shown to possess an imino methyl group. Of the 8 atoms of oxygen, 4 were shown in a previous communication to be present in a methylenedioxy and two methoxy groups, the remaining 4 are now proved to be present as OH groups. A comparison of the properties, absorption curves and derivatives of umbellatine with those of berberine has been made; it has been concluded that methylenedioxy-tetrahydroisoquinoline skeleton forms a part of the umbellatine nucleus.

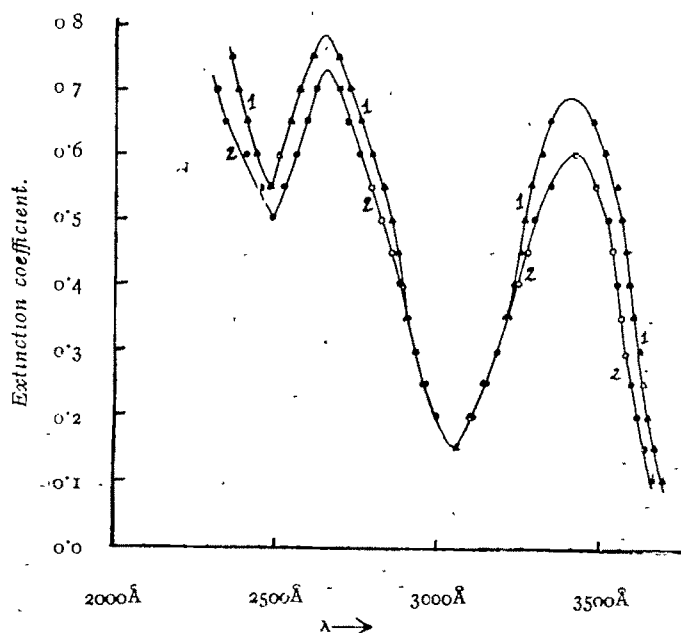
Umbellatine is mentioned to be the chief alkaloid of the Himalayan *Berberes*, e.g., *B. insignis*, *B. nepalensis*, *B. lycium* and *B. Wallichiana* etc., and some of its salts are described.

Umbellatine, the alkaloid first isolated from *Berberis umbellata*, Wall (J. Indian Chem Soc., 1940, 17, 289) is found to be present as the major alkaloid in other Himalayan *Berberes*. It has been reported to occur in *B. insignis* Hook. f. (Chatterjee, J. Amer. Pharm. Assoc., 1941, 30, 247) and also in other species of the Himalayan *Berberes* like *B. nepalensis* Spreng., *B. lycium* Royle and *B. Wallichiana* D.C., an account of which has not yet been published. Berberine is the chief alkaloid of all European *Berberes*, investigated up till now, and since umbellatine is observed to occur commonly in the Himalayan species of the same genus *Berberis*, it is thought that most probably umbellatine is analogous to berberine in structure. A comparative study of the properties and derivatives of both umbellatine and berberine shows the close similarity of the two alkaloids (Table I).

In Fig. 1 are shown the near ultraviolet absorption curves of umbellatine and berberine. It is well known that such comparison of spectra serves as one of the physical methods to arrive at the essential central structure of complex organic compounds (Hartley, *Phil. Trans.*, 1885, 176A, 471; Dobbie, J. Chem. Soc., 1903 83, 605; Brustier, *Bull. Soc. Chim.*, 1926, 39, 1527). It is evident from the figure that the absorption curves of these two alkaloids are extremely analogous. Only a slight hyperchromic effect is observed in the new base which might easily be attributed to the several phenolic OH groups it contains (Klingstedt and Brode, International Critical Tables). Kitasato's work (*Acta Phytichim.*, 1927, 3, 175) on the absorption spectra of 42 alkaloids classifies the bases berberine, coptisine,

cotarnine, worenine and hydrastinine as showing very similar absorption spectra. They all show the strong band at *ca.* 3400-3500Å, which the author connects with the methylenedioxy tetrahydroisoquinoline skeleton by a process of elimination. The identical position of this prominent band in umbellatine is a strong positive evidence for the presence of the same basic nucleus in this alkaloid, the evidence being of course as conclusive as is warranted by this statistical physical method of structure analysis.

FIG. 1.



Curves 1 & 2 refer respectively to berberine and umbellatine

Umbellatine forms salts with acids like hydrochloric, hydriodic, nitric, sulphuric and picric acids mostly analogous to the corresponding salts of berberine, in their colour and solubility in water. With palladium-charcoal, umbellatine takes up successively 2 and 4 atoms of hydrogen, forming a yellow dihydroumbellatine and a lemon-yellow tetrahydroumbellatine, m.p. 213-15° (decomp.). It had been already shown that umbellatine formed a yellow coloured, bright crystalline derivative with nitrous acid. From the estimation of nitrogen of the derivative, it was supposed to be a nitroso compound which pointed to the secondary character of the nitrogen atom in umbellatine. The analytical data are also in good

agreement with the formula $C_{21}H_{21}O_8N$, HNO_2 , where nitrous acid forms the nitrite of the base. It is not improbable, therefore, that the N atom in umbellatine molecule might be present as a tertiary amine. More than one example of alkaloids might be cited where a molecule of nitrous acid is added to the tertiary nitrogen group. The phenylthiocarbamide test for the secondary nitrogen fails in the case of umbellatine. The base forms a methiodide and its imino-methyl determination (Herzig and Meyer) is positive, elucidating the tertiary nature of the N atom of the base; so the molecular formula of umbellatine $C_{21}H_{21}O_8N$, can be extended to $C_{20}H_{19}O_8 (N \cdot CH_3)$.

The product of methylation of the base by diazomethane could not be isolated; the methylating agent methyl iodide reacted only to form a methiodide; umbellatine could only be successfully methylated by dimethyl sulphate, producing a monomethyl ether, which indicates the phenolic character of one of the hydroxyl groups present. On boiling with acetic anhydride in presence of a few drops of pyridine, umbellatine yields a diacetyl derivative. Of the 8 oxygen atoms present, in one molecule of the base, 6 can now be accounted for—2 of them are in the methylenedioxy group and 2 in the methoxy groups in the molecule as has been previously recorded. The remaining 2 which are acetylated must be present in two free hydroxyl groups. Now the formula of umbellatine is further extended to $C_4H_8O_2 (CH_2O_2) (NCH_3) (OMe)_2 (OH)_2$. The function of the remaining 2 oxygen atoms of the molecule could not be determined directly as yet. Umbellatine does not undergo hydrolysis in presence of an acid or an alkali, eliminating the possibility of the 2 oxygen atoms being present in a lactone ring. Unlike berberine, it would neither form an oxime nor a semicarbazone which, in all probability, indicates the absence of a carbonyl group. The base contains 4 reactive hydrogen atoms (Zerewitinoff). It has already been mentioned (*loc. cit.*) that umbellatine retains half a molecule of water of crystallisation even when dried in *vacuo* over P_2O_5 at 110° . The experimental results show that the volumes of methane collected during the active hydrogen determinations are always greater than the calculated volumes. There the excess volume of methane can safely be considered to be formed from half a molecule of water reacting with magnesium methyl iodide, so the 4 atoms of hydrogen have been, in all probability, obtained from 4 hydroxyl groups of the base, 2 of which could be acetylated. Hence the formula of umbellatine can be written as :

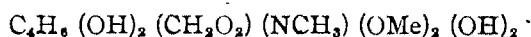


TABLE I.

Comparison of properties of umbellatine and berberine and their derivatives.

| | Umbellatine. | Berberine. |
|---|---|--|
| Mol. formula | $C_{21}H_{21}O_5N$ | $C_{20}H_{19}O_5N$ |
| Colour | Yellow | Yellow |
| M.p. | 206-7° (decomp) | 145° |
| Water of crystallisation | 5.5 molecules; $\frac{1}{2}$ molecule is retained even on drying in <i>vacuo</i> at 110°. | 5.5 molecules; $2\frac{1}{2}$ molecules are retained on drying at 100°. |
| Solubility | Soluble in ethyl and methyl alcohols, sparingly soluble in acetone, chloroform and cold water. Insoluble in benzene. | Soluble in ethyl and methyl alcohols, sparingly soluble in acetone and chloroform, more soluble in water. Slightly soluble in benzene. |
| Optical activity | Inactive | Inactive |
| Acidified with conc H_2SO_4 and brought in contact with chlorine water. | A blood-red ring at the junction of the layers of two liquids. Umbellatine chloroplatinate cannot be crystallised. | A blood-red ring at the junction of the layers of two liquids. Berberine chloroplatinate can be crystallised from boiling amyl alcohol. |
| Functional groups | Contains 2 methoxy groups, 1 methylenedioxy group. Contains at least two active hydroxyl groups. Contains an imino-methyl group Does not form an oxime | Contains 2 methoxy groups, 1 methylenedioxy group. Does not contain any hydroxyl group. Contains an imino group. Forms an oxime under certain conditions. |
| Tetrahydro derivatives | Tetrahydroumbellatine Lemon-yellow plates, rystalline, m.p. 213-15° (decomp.) | Tetrahydroberberine Crystalline, colourless prismatic needles m.p. 262° (decomp.). |
| Salts of the type B, HX with mineral acids. | Umbellatine, HCl etc. | Berberine, HCl etc. |

EXPERIMENTAL.

Absorption Spectra of Umbellatine and Berberine.—Solutions of the bases having a concentration of 1 in 80,000 in water were used.

Tungsten steel spark was the source of light. The spectra were photographed with a Spekker spectrophotometer on a quartz spectrograph. The match points were marked by visual comparison and the wave-lengths read off approximately from a wave-length reading plate slipped behind the negative. Both the curves show two absorption maxima at 2650 and 3430, minima at 2490 and 3050 Å. (FIG. 1)

Umbellatine nitrate, prepared by the usual method, crystallised from alcohol as dull yellow needles. It charred without melting above 250°. (Found: N, 6.3. $C_{21}H_{21}O_8N$, HNO_3 requires N, 6.0 per cent).

Umbellatine sulphate, prepared by the usual method, crystallised from hot alcohol as glistening yellow needles, m.p. 274° (decomp.). [Found: S, 3.2. $(C_{21}H_{21}O_8N)_2H_2SO_4$ requires S, 3.4 per cent].

Umbellatine Picrate.—On treating a solution of umbellatine in alcohol with an alcoholic solution of picric acid, the picrate was precipitated at once. The picrate was crystallised from hot alcohol as brown feathery needles, m.p. 232° (decomp.). (Found: N, 8.9. $C_{27}H_{24}O_{15}N_4$ requires N, 8.7 per cent).

Tetrahydroumbellatine.—A solution of umbellatine base (0.23 g.) in methyl alcohol (20 c.c.) was mixed with palladium-charcoal catalyst (0.1 g.) and shaken with hydrogen until the yellow solution was practically colourless. Absorption was at first rapid but became slower after 20 minutes; 23 c.c. of hydrogen were absorbed in 45 minutes (Calc. for $C_{21}H_{21}O_8N$, $\frac{1}{2} H_2O$: 4 H, 25 c.c.). The solution was filtered from the charcoal; the charcoal was washed carefully with methyl alcohol (10 c.c.). The solution deposited on concentration a pale yellow powder which on recrystallisation yielded lemon-yellow transparent plates of tetrahydroumbellatine, m.p. 213–15° (decomp.). (Found: C, 59.5; H, 5.5; N, 3.3. $C_{21}H_{25}O_8N$ requires C, 60.0; H, 6.0; N, 3.34 per cent).

Dihydroumbellatine.—A solution of umbellatine (0.2 g.) in methyl alcohol (20 c.c.) was shaken with palladium-charcoal catalyst (0.1 g.) in hydrogen. Absorption was stopped after 20 minutes when 11 c.c. of hydrogen (equivalent to 2 atoms) had been taken up. The solution of the product was filtered from the catalyst and was concentrated to yield dihydroumbellatine as dull yellow rods, which charred without melting. (Found: C, 60.0; H, 5.34. $C_{21}H_{23}O_8N$ requires C, 60.43; H, 5.5 per cent).

The Imino-methyl in Umbellatine.—The imino-methyl was determined by the micro Herzig-Meyer method. (Found: N'Me, 5.3. $C_{21}H_{21}O_8N$, $\frac{1}{2} H_2O$ requires N'Me, 6.8 per cent).

Umbellatine Monomethyl ether.—An excess of dimethyl sulphate was added drop by drop to a solution of umbellatine (0.1 g.) in 10% potassium

hydroxide with constant shaking. After $\frac{1}{2}$ hour yellow, silky fine needles separated. The shaking and the addition of dimethyl sulphate were continued and the mixture was kept alkaline. After an hour the crystals were filtered, well washed with water, dried and then crystallised from alcohol as silky yellow needles, m.p. 265° . [Found OMe, 21.1. $C_{21}H_{20}O_8N$ (OMe) requires, OMe 20.9 per cent; equiv. to 3 OMe groups of which 2 are already present in a molecule of umbellatine].

Diacetylumbellatine.—Umbellatine (0.1 g.) was mixed with acetic anhydride (20 c.c.) and pyridine (6 to 8 drops) and heated on a water-bath till the last traces of umbellatine went completely into solution, the time usually taken being $3\frac{1}{2}$ hours. On leaving overnight, yellow needles appeared which shrink at 187° and melt with decomposition at 193° . (Found: C, 59.72; H, 5.84; N, 2.98. $C_{23}H_{23}O_{10}N$ requires C, 59.8; H, 5.4; N, 2.8 per cent).

Reactive H atoms in Umbellatine.—A Zerewitinoff determination of the base liberated methane equivalent to 4 reactive hydrogen atoms.

0.48 G. of umbellatine, $C_{21}H_{21}O_8N$, $\frac{1}{2} H_2O$, in pyridine treated at the ordinary temperature for 10 minutes with excess of methyl magnesium iodide, gave 13.2 c.c. of methane (theory requires 11.2 c.c. of methane, equiv. to 4 reactive hydrogen atoms).

0.454 G. of umbellatine gave 12.3 c.c. of methane (theory requires 10.6 c.c. of methane; equiv. to 4 reactive hydrogen atoms).

0.38 G. of umbellatine gave 10.4 c.c. of methane (theory requires 7.8 cc. of methane; equiv. to 4 reactive hydrogen atoms).

The author expresses his gratefulness to the Rector, the very Rev. Father C. A. Vrithoff, S.J., for affording him laboratory facilities, to Mr. G. Karmakar, M.Sc., for the absorption photographs and to Mr. N. Ghosh, M.Sc. for all the micro-analyses, recorded in this paper.

ST JOSEPH'S COLLEGE,
DARJEELING.

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STUDIES IN INDIGOID DYES. PART X.

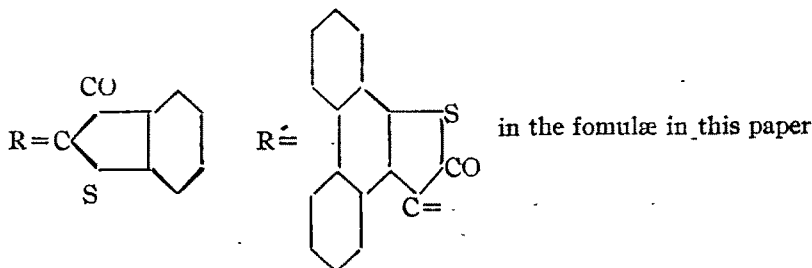
BY PARĀSH CHANDRA DUTTA AND RAMANI MOHAN SINHA.

Indigoid dyes derived from 9-phenanthrathiophene-2:3'-dione have been described.

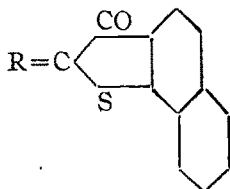
9-Phenanthrathiophene-2':3'-dione (*J. Indian Chem. Soc.*, 1941, **18**, 471) has been condensed with thioindoxyl and with isomeric benzthioindoxyls such as 6:7, 4:5 and 5:6 with a view to studying the influence of the position of additional benzene ring in the thionaphthene nucleus on the colour of these indigoid dyes. The parent substance, the condensation product of the dione with thioindoxyl, is a violet dye and the condensation products with 6:7- and 4:5-benzthioindoxyls are chocolate dyes and the product with 5:6-compound, a bluish violet dye. This is in conformity with the findings of one of the present authors (Dutta, *Ber.*, 1934, **67**, 1319; 1935, **68**, 1447; 1936, **69**, 2343) that, if an additional benzene ring is introduced in the thionaphthene nucleus to load the molecule, the most favourable position for the deepening effect on colour is the 5:6-position; on the other hand 4:5 and 6:7-positions have a lightening effect.

EXPERIMENTAL.

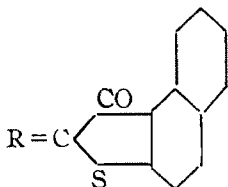
3':9-Phenanthrathiophene-2-thionaphthene-indigo.



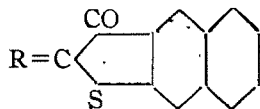
9-Phenanthrathiophene-2':3'-dione (0.66 g.) was dissolved in acetic acid (50 c.c.) and 0.35 g. hydroxythionaphthene in 10 c.c. acetic acid. Into the separate solutions a current of carbon dioxide was passed for sometime and then the solutions were mixed together. The mixed solution was refluxed in a current of carbon dioxide with the addition of 5 c.c. of concentrated hydrochloric acid when it became dark brown and a reddish violet crystalline mass separated out. It was filtered, the precipitate collected and washed with acetic acid and water. It was then recrystallised from pyridine in violet slender needles, melting above 290°. The dye dissolves in an alkaline hydrosulphite vat with a yellow colour and dyes cotton a violet shade. (Found: C, 72.56; H, 3.21. $C_{24}H_{12}O_2S_2$ requires C, 72.72; H, 3.03 per cent).

3':9-Phenanthrathiophene-2-(6:7)-benzthionaphthene-indigo

was prepared like the previous compound from 9-phenanthrathiophene-2':3'-dione (0.66 g.) and 6:7-benzthioindoxyl (0.5 g.). It was recrystallised from nitrobenzene in small chocolate needles, melting above 295°. It dissolves in concentrated sulphuric acid with a brownish violet colour and in alkaline hydrosulphite with a yellowish brown colour from which it dyes cotton a dark chocolate shade. (Found: C, 74.98; H, 3.21. $C_{28}H_{14}O_2S_2$ requires C, 75.33; H, 3.14 per cent).

3':9-Phenanthrathiophene-2-(4:5)-benzthionaphthene-indigo

was prepared in a way similar to the previous compounds from 9-phenanthrathiophene-2':3'-dione (0.66 g.) and 4:5-benzthioindoxyl (0.5 g.). It was obtained as a chocolate crystalline mass from nitrobenzene, m. p. above 295°. It dissolves in concentrated sulphuric acid with a blue colour and dyes cotton from an orange-yellow hydrosulphite vat a chocolate shade. (Found: C, 75.14; H, 3.19 per cent).

3':9-Phenanthrathiophene-2-(5:6)-benzthionaphthene-indigo

was prepared similarly from 9-phenanthrathiophene-2':3'-dione and 5:6-benzthioindoxyl. It was recrystallised from nitrobenzene in violet needles, melting above 295°. It dissolves in concentrated sulphuric acid with a blue colour and dyes cotton from an alkaline hydrosulphite vat a blue shade. (Found: C, 75.21; H, 3.16 per cent).



STUDIES IN GLASS SYSTEMS. REFRACTOMETRIC MEASUREMENTS OF POLAR CRYSTALS IN B_2O_3 -GLASS.

BY SUBODH KUMAR MAJUMDAR AND ASEEM KUMAR SARMA.

The mole refraction of LiCl, NaCl, KCl, RbCl and CsCl dissolved in boric oxide glass has been measured and the deformation of the crystals calculated.

Fajans and Joos (*Z. Physik*, 1921, 97, 304) postulated the mutual effect of neighbouring ions in polarising their electron sheaths. Certain regularities have been observed by Fajans and his co-workers in various systems, viz., solid crystalline state, aqueous solution and in the gaseous state. An excellent summary of the experimental results in aqueous solution has been given by Fajans and others (*Z. Elektrochem.*, 1928, 34, 2). Although much work has been done on the above lines comparatively little work has been done in studying the deforming effect of typical polar crystals when dissolved in a homogeneous glass, preferably not exerting any chemical action. Wulff and Majumdar (*Z. physikal. Chem.*, 1936, 31B, 319) studied the system xNa_2O, yB_2O_3 . The subject has also been studied by Tilton and Tool (*Bureau of Standards J.*, 1929, 8, 619), Faik and Finn (*ibid.*, 1931, 6, 993), Hubbard and Finn (*ibid.*, 1935, 14, 133) and Morew and Merwin (*J. Opt. Soc. Amer.*, 1932, 22, 632).

Recently Biltz and his co-workers have carried out a systematic investigation on the subject of additivity of constituents in the glass system (Biltz, Weibke and Schraeder-Träger, *Z. anorg. Chem.*, 1937, 234, 253) and have concluded that strict additivity still persists when constituents enter into the composition of a glass system : "Die Molrefraktion einfacher Gläser ist eine eindeutig und streng additive Grösse." (*Glastech. Ber.*, 1938, 16, 131). Kordés (*Z. anorg. Chem.*, 1939, 241, 1, 418), on the other hand, disputes the above conclusion of Biltz. It was therefore decided to prepare solid solutions of polar crystals like LiCl, NaCl, KCl, RbCl and CsCl in boric oxide glass and measure the refractive index and density of the samples and hence calculate the deformation produced in the crystals.

Various methods have been suggested for determining the deformation of ions and molecules, based on measurement of dielectric constant, refractive index, etc. It is well known that in the Clausius-Mosotti equation, if

the dielectric constant is replaced by square of the refractive index (for infinitely long waves), then we get the Lorenz and Lorentz equation

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d},$$

where r is the specific refraction. By multiplying both sides of this equation by M , the molecular weight, we get R , the mole refraction, given by the equation

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

R , which is expressed in c.c., is a measure of the molar polarisation (electron polarisation if measurements are made with the visible range of the spectrum).

It is well known that paths of electrons undergo change when brought in an external electric field, the magnitude of the deviation depending upon strength of the applied field (Stark effect). It is natural to expect, therefore, that when the electron sheath of an ion and also to a limited extent of neutral molecules comes in the vicinity of another ion, a deformation should occur, which may be likened to the Stark effect in a homogeneous field. The deformation, which really represents a sum total effect of various factors, is at best only a qualitative indication of mutual interaction of charged particles in the system. In some cases, the phenomenon has been quantitatively explained in the light of the more recent theory of resonance, as for example in the case of the HCl molecule, but up till now, no general quantitative explanation is available. Fajans and his co-workers have deduced certain regularities guiding deformation in general. The cation is usually the deforming and the anion the deformed ion. Actually there are several effects to be taken in account, namely the mutual interactions of the respective nuclei and the peripheral charges. These effects are, however, not all equally strong and we are left with the one effect which preponderates over the rest, namely, the deforming effect of the negative sheath of the anion by the positive sheath of the cation. It follows, therefore, that with the same anion, a smaller radius of the cation of the same valency will mean a stronger deformation of the anion and this will of course increase with higher valency of the cation. The general conclusions of Fajans and Joos may be briefly summarised as follows: (i) The deformability of ions increases with increasing atomic number. (ii) An anion is more deformable than the cation; the greater the charge of the ion, the greater the deformation. (iii) The deforming power of the cation increases with the charge and diminishes with the ionic diameter.

If τ represents the specific refraction of a mixture of, say, two components, whose mole refractions in the pure state are τ_1 and τ_2 and p , the percentage of the first component in the mixture, then, if there is no mutual interaction of the components in the mixture, the additivity law will hold good, i.e.,

$$100\tau = p\tau_1 + (100-p)\tau_2.$$

Any deviation from the additivity formula will point to deformation in the system. If the solvent be assumed to be unaffected, which probably is not strictly true, the deviation from the additivity formula will afford us a means of at least qualitatively defining deformation of the solute.

In a system consisting of $p\%$ of XCl and $(100-p)\%$ of B_2O_3 , if we determine the refractive index n_D for sodium light and the density d of the system, then we can calculate the value of τ_2 from the above equation after finding out the value of τ for the mixture from the Lorenz-Lorentz equation, taking a constant value of τ_1 , which is taken to be 0.151 c.c. (Wulff and Majumdar, *loc. cit.*). By multiplying this value of τ_2 by the molecular weight of XCl , we get the mole refraction of XCl in the glass. This value may be usefully compared with those of XCl in the crystal on the one hand and in state of infinite dilution in aqueous solution on the other.

For absolute value of R , an extrapolated value of refractive index, n_∞ , should be used in the Lorenz-Lorentz equation. But for comparative purpose in which absolute values are not involved, the value of refractive index n_D for sodium light may be conveniently used.

EXPERIMENTAL.

Preparation of the Samples—Boric oxide (Merck *p.10 Analyse* quality) was twice recrystallised from hot water and dried in a vacuum desiccator for 7 days until absolutely anhydrous as tested by anhydrous copper sulphate with its solution in absolute alcohol. Unless special precautions are taken in dehydration, the molten B_2O_3 glass will tenaciously retain traces of moisture, which would later interfere with the value of a mole refraction, R . A better method, which could not unfortunately be followed, would be to use an induction oven of high frequency in high vacuum (10^{-4} to 10^{-6} mm), using an ordinary oil pump and a couple of secondary mercury diffusion pumps, as used by Wulff and Majumdar (*loc. cit.*). The error involved; however, is not regarded sufficiently high to affect comparative results which the present communication claims.

The chlorides of lithium, sodium, potassium, rubidium and caesium were Merck's reagent quality products and were carefully dehydrated for a pretty long time. Lithium chloride, which is very hygroscopic, was evaporated to dryness in a platinum dish and maintained at a temperature of 400-500° in an electric oven for several hours.

Samples of boric oxide and alkali chloride in varying proportions were taken in platinum crucible and heated in an electric furnace at a temperature of 900-1000° for several hours in order to ensure thorough homogeneous mixing of the ingredients. A portion was sublimed at first but after a time a melt of constant composition was obtained. The crucible was then removed from the furnace and quickly chilled by placing it on a cool surface, when the solidified glass cracked. The solid was then taken out with the help of a sharp-pointed knife, transferred to a sample tube and kept within a vacuum desiccator. Before each experiment the sample was first dipped in absolute alcohol, then in pure toluene and finally quickly dried in a blast of hot air. In this way any superficial layer of hydroxide formed was washed out and the glass presented a thoroughly transparent appearance.

The above method of preparation of samples is not free from objection. Molten boric oxide has a different coefficient of cubical expansion from platinum and in consequence of this when the melt solidifies great stress is brought to bear upon the system. This might render the glass double diffracting, a fact which can be easily verified by suspending the solid in a liquid and examining it in a polarisation microscope with crossed nicols. Each sample was examined in this way before further optical examination and only those pieces, which remained dark in all positions with crossed nicols, were selected.

Analysis of the Samples.—A weighed amount of the anhydrous sample was taken in a weighed platinum crucible, treated repeatedly with a mixture of hydrofluoric and sulphuric acids (both of Merck's reagent quality) and was first evaporated on asbestos to drive off boron trifluoride and then strongly ignited over Mecker burner; the residue was cooled in a desiccator and weighed as alkali sulphate. In this way, the amount of alkali chloride was calculated and by subtracting this weight from the original weight of the glass, the proportion of boric oxide was determined.

Density Determination —It is well known that density of solids cannot be determined with the same degree of accuracy as in the case of liquids. Different investigators have tried to determine the density of solids by the pyknometer method using liquids of high density as thallium ethylate, solu-

tion of soluble iodide of mercury and potassium, methylene iodide, acetylene tetrabromide, various borotungstate solutions, etc.

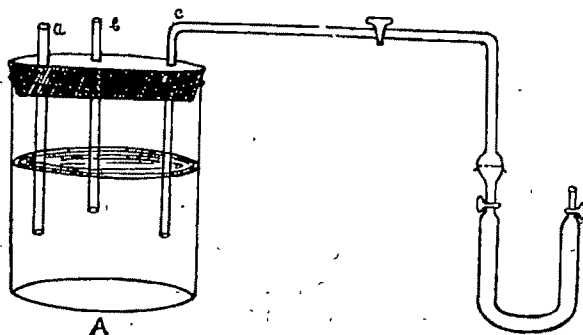
Day and Allen (*J. Amer. Chem. Soc.*, 1906, **28**, 37) using a pycnometer of about 25 c.c. capacity containing 5-10 g. of solid substance obtained satisfactory results, the error not exceeding one unit in the fourth decimal place. But the method has not proved satisfactory in the case of smaller particles and was therefore modified by Johnston and Adams (*J. Amer. Chem. Soc.*, 1912, **34**, 566). The pycnometer method thus requires special modification for determining crystal densities. Lord Berkeley (*J. Chem. Soc.*, 1907, **91**, 56) obtained satisfactory results by using carbon tetrachloride as the immersion liquid. Baxter and Wallace (*J. Amer. Chem. Soc.*, 1916, **38**, 259) used toluene as the floatation medium but the method did not give reproducible results, the error being in the region of 5%.

The technique of the floatation method was first developed by Rétger (*Z. physikal. Chem.*, 1889, **3**, 289) and later by Wulff and Heigl (*Z. physikal. Chem.*, 1931, **153A**, 187). The floatation method is in general superior to the immersion method for determination of crystal densities. The method is worked on the principle that a solid will only just float at all points of a liquid only if it has the same density as the liquid itself. The range of densities covered by this method depends on the densities of liquids available as standard liquids. Acetylene tetrabromide and methylene iodide are particularly suitable for use as the heavy liquids and benzene or toluene, carefully dehydrated, may be used as the light standard liquid. Methylene iodide has an approximate density of 3.5 and by diluting it with benzene the density of the mixture may be reduced to 0.9. Acetylene tetrabromide, which has a density of about 2.96, can also be conveniently used for density determinations. The method is quite accurate if the temperature of the liquid mixture is carefully controlled. The chief error of the method lies in the adherence of a thin layer of air to the surface of the sample. As a result of this, when a powder consisting of small particles is used, at a certain point some particles will be found to rise and others to fall at the same time. But in spite of this error, density determined by the floatation method is correct up to 5 in the fourth place of decimals. A simplified method analogous to that used by Wulff and Heigl (*loc. cit.*) has been used in this investigation.

In the present investigation, acetylene tetrabromide (Merck), redistilled under reduced pressure and redistilled toluene, previously dried over metallic sodium, have been used as the heavier and lighter liquid respectively. A large weighing bottle A (100 c.c.) fitted with a specially made ground glass stopper was suspended in a transparent thermostat maintained at $35^{\circ} \pm 0.5$.

The stopper has three openings, *a*, for introducing the lighter liquid, *b*, for introducing a current of air under pressure and *c*, for forcing the liquid into the pyknometer. The end of the tube *c* is fitted by ground glass joint into one of the side-tubes of a specially made pyknometer (capacity about 24 c.c.). The pyknometer had two glass stop-cocks, which were made air-tight by using the minimum amount of a paste of dextrin in glycerine, which had been found to be best suited for the purpose. The actual procedure, including removal of excess of liquid sticking to the inside of open tubes above the stop-cocks is very important for the purpose of getting reproducible results. After cleaning the pyknometer in the usual way, it was dried by suction and the minimum quantity of white vaseline was used in the stop-cocks; any excess of it, outside the stop-cocks and within the protruding tube was carefully wiped off repeatedly with clean linen and rolled filter paper. It was then weighed empty using a dummy counterpoise of approximately the same shape and size to correct for buoyancy and moisture. Both the pyknometer and the dummy were left in the balance for a sufficiently long time to ensure full deposition of moisture under the conditions. The pyknometer was then filled with distilled water, placed in the thermostat and a similar procedure was followed before weighing. As the liquids used in the method dissolved vaseline, the dextrine paste in glycerine was used instead and the weight of the empty pyknometer determined again in a similar manner.

FIG. 1.
Suspension vessel and pyknometer.



About 50 c.c. of acetylene tetrabromide were taken in vessel *A* (Fig. 1), placed in the thermostat and a piece of tested glass previously treated was dropped into it. The latter usually floated up on account of its lower density. Purified toluene was now gradually introduced through the opening *a*, drop by drop and the solution stirred by bubbling dry air through *b*. In this way a point was reached at which the particle remained suspended within the mixture in any position. The method is quite sensitive and one or two drops

of either liquid reverses the course of the particle, the exact point being determined by adding forwards and backwards several times until the desired point was reached. The ground end of the pyknometer tube was next joined to the end of the side-tube, *c*, of the suspension vessel. Both the stop-cocks of the pyknometer were then opened, the side-tube, *a*, closed and air was blown through *b*, until the pyknometer was filled. The connection with the side-tube was next broken and the pyknometer allowed to remain in the thermostat for some more time. The usual precautions were taken before weighing the pyknometer. Two independent measurements were made with each sample and the mean value of density taken.

Determination of the Refractive Index.—The refractive index determination of crystals and small pieces of glass is a matter of considerable difficulty. The Pulfrich refractometer, which is excellently suited for liquids, can be used with transparent solids, if the latter is carefully ground so as to give it the shape of a right-angled prism. It was then placed directly on top of the prism of the instrument and the measurement is carried out in the same way as in the case of a liquid. As boric oxide is hygroscopic even in the solidified state of glass, although much less than in the non-fused solid state, this method could not be employed. It is also difficult to realise experimentally optically plane ground surfaces. Another method, the best so far proposed, is due to Wulff and Heigl (*loc. cit.*). According to this method a fine pencil of homogeneous light is made to undergo interference through a fine slit. One part of the interfered ray passes through the solid suspended in a liquid and the other part through the suspension medium, which is contained in a glass trough provided with plane parallel sides. In consequence of difference in refractivity of the solid and the liquid, the interference bands which are observed through a telescope on the other side are bent. Two liquids are chosen, one having a slightly higher and the other a slightly lower refractive index than the solid and the composition of the suspending medium gradually changed until the interference bands become again straight. At this point the liquid mixture and the solid have the same refractivity. With a specially constructed refractometer, the refractive index of the former is measured from above. In the present investigation the refractive index of the glasses have been measured by the Becke method. A source of error which could not unfortunately be eliminated lay in the fact that the density determinations were carried out at 35°, whereas the refractive indices were determined at the room temperature. Properly speaking a correction factor has to be applied for difference of temperature. As is well known, however, the temperature coefficient of refractive index is smaller than the experimental error of the method and for comparative results the error will not be

appreciable. The Becke method is based on the principle of total reflection of light passing from a denser to a rarer medium when the incidence is outside the critical angle. The method was first used for crystals by Schröder von der Kolk ("Kurze Anleitung zur mikroskopischen Kristallbestimmung", Wiesbaden, 1898). It consists in making the refractive index of a liquid mixture agree as far as possible with that of a fragment of a crystal immersed in it by altering its composition and then determining the refractive index of the mixture by the usual method. Small fragments of the glass were placed in a trough mounted on a slide and covered with one of two selected liquids. It follows from optical considerations that if on raising the eye-piece of the microscope after focussing the object, the bright lines of contact tend to go out of the solid, then the liquid has a higher refractivity than the solid. On the other hand, if on raising the eye-piece, the lines of contact appear to converge within the solid, the reverse is the case. Drops of the second liquid were then added to the first and the object viewed in a dark room illuminated by sodium light. In this way two liquid mixtures were obtained for the same sample of glass, one possessing a slightly higher and the other a slightly lower refractive index than the sample. These mixtures were then examined in an ordinary Pulfrich refractometer in sodium light and the mean of the two values taken. Usually the variation

TABLE I.

| System: LiCl—B ₂ O ₃ | | | System: RbCl—B ₂ O ₃ | | |
|--|----------|----------------|--|----------|----------------|
| LiCl | Density. | n _D | RbCl | Density. | n _D |
| 14.35% | 1.9586 | 1.4515 | 28.96% | 2.1445 | 1.4657 |
| 20.43 | 2.0052 | 1.4495 | 38.20 | 2.2226 | 1.4523 |
| 25.79 | 2.0392 | 1.4480 | 45.74 | 2.2664 | 1.4374 |
| System: CsCl—B ₂ O ₃ | | | 47.13 | 2.2762 | 1.4342 |
| CsCl | Density. | n _D | 52.12 | 2.3425 | 1.4313 |
| 44.07% | 2.4683 | 1.5234 | System: NaCl—B ₂ O ₃ | | |
| 52.72 | 2.6534 | 1.5401 | | | |
| 57.48 | 2.7725 | 1.5525 | System: KCl—B ₂ O ₃ | | |
| KCl | Density. | n _D | NaCl | Density. | n _D |
| 25.32% | 2.0441 | 1.4843 | 30.63% | 2.0321 | 1.4684 |
| 48.86 | 2.0524 | 1.4665 | 35.64 | 2.0385 | 1.4630 |
| 56.31 | 2.0536 | 1.4584 | 38.07 | 2.0422 | 1.4585 |
| 68.64 | 2.1045 | 1.4542 | 47.92 | 2.0556 | 1.4470 |

was in the fourth place of decimals, which for solids may be regarded as satisfactory. The following liquids were used for the purpose: toluene, carbon tetrachloride and purified kerosene oil. Before proceeding with any piece it was tested in the polarisation microscope to see whether it was doubly diffracting or not, and only those pieces were taken which were optically isotropic.

In the following tables the values of r_{LiCl} and hence R_{LiCl} for the alkali chloride are calculated from the mixture law; the respective values of R at infinite dilution in aqueous solution and in crystal are shown in the last column. The value of r for B_2O_3 is taken as 0.151 (Wulff and Majumdar, *loc. cit.*).

TABLE II.

System: $\text{LiCl}-\text{B}_2\text{O}_3$.

| LiCl. | $r_{\text{mix.}}(\text{exp.})$ | $r_{\text{LiCl}}(\text{calc.})$ | $R_{\text{LiCl}}(\text{calc.})$ | $R_{\text{sol.}}$ | $R_{\text{cryst.}}$ |
|--------|--------------------------------|---------------------------------|---------------------------------|---|---------------------|
| 14.35% | 0.1375 | 0.0571 | 2.42 | 8.76 | 7.59 |
| 20.43 | 0.1339 | 0.0675 | 2.86 | Fajans, Kohnner and Geffcken (<i>Z. Elektrochem.</i> , 1925, 34, 2). | |
| 25.79 | 0.1313 | 0.0748 | 3.17 | | |

TABLE III.

System: $\text{NaCl}-\text{B}_2\text{O}_3$.

| NaCl. | $r_{\text{mix.}}(\text{exp.})$ | $r_{\text{NaCl}}(\text{calc.})$ | $R_{\text{NaCl}}(\text{calc.})$ | $R_{\text{sol.}}$ | $R_{\text{cryst.}}$ |
|--------|--------------------------------|---------------------------------|---------------------------------|---|---------------------|
| 30.63% | 0.1369 | 0.1051 | 6.14 | 9.27 | 8.52 |
| 35.64 | 0.1351 | 0.1064 | 6.21 | Fajans, Kohnner and Geffcken (<i>loc. cit.</i>). | |
| 38.07 | 0.1337 | 0.1060 | 6.22 | | |
| 47.92 | 0.1300 | 0.1072 | 6.26 | | |

TABLE IV.

System: $\text{KCl}-\text{B}_2\text{O}_3$.

| KCl. | $r_{\text{mix.}}(\text{exp.})$ | $r_{\text{KCl}}(\text{calc.})$ | $R_{\text{KCl}}(\text{calc.})$ | $R_{\text{sol.}}$ | $R_{\text{cryst.}}$ |
|--------|--------------------------------|--------------------------------|--------------------------------|--|---------------------|
| 25.32% | 0.1399 | 0.1074 | 8.41 | 11.31 | 10.833 |
| 48.86 | 0.1349 | 0.1140 | 8.52 | Wulff and Schaller (<i>loc. cit.</i>). | |
| 56.31 | 0.1309 | 0.1154 | 8.61 | | |
| 68.64 | 0.1275 | 0.1168 | 8.72 | | |

TABLE V.

System: $\text{RbCl}-\text{B}_2\text{O}_3$.

| RbCl. | $r_{\text{mix.}}(\text{exp.})$ | $r_{\text{RbCl}}(\text{calc.})$ | $R_{\text{RbCl}}(\text{calc.})$ | $R_{\text{sol.}}$ | $R_{\text{cryst.}}$ |
|--------|--------------------------------|---------------------------------|---------------------------------|---|---------------------|
| 28.96% | 0.1288 | 0.0743 | 8.98 | 12.84 | 12.55 |
| 38.20 | 0.1215 | 0.0740 | 8.96 | Wulff and Schaller (<i>loc. cit.</i>) | |
| 45.74 | 0.1157 | 0.0739 | 8.94 | | |
| 47.13 | 0.1146 | 0.0738 | 8.93 | | |
| 52.12 | 0.1106 | 0.0736 | 8.90 | | |

TABLE VI.

| System: CsCl—B ₂ O ₃ . | | | | | |
|--|---------------------------|----------------------------|----------------------------|--------------------------------------|---------------------|
| CsCl. | $r_{\text{mix.}}$ (exp.). | r_{CsCl} (calc.). | R_{CsCl} (calc.). | $R_{\text{sol.}}$ | $R_{\text{cryst.}}$ |
| 44.07% | 0.1239 | 0.0897 | 15.10 | 15.60 | 15.30 |
| 52.72 | 0.1183 | 0.0891 | 15.00 | Wulff and Heigl (<i>loc. cit.</i>) | |
| 57.48 | 0.1153 | 0.0890 | 14.99 | | |

DISCUSSION.

It is interesting to discuss how far the mole refraction of alkali chlorides in solid solution in a medium of high viscosity like B₂O₃, calculated from the additivity formula, on the assumption that the mole refraction of the solvent remains constant, tally with those found for infinite dilution in aqueous solution on the one hand and the value in crystals of the pure salts on the other. The value of R in the crystal is in every case, as may be easily expected, less than that in aqueous solution at infinite dilution for obvious effects of deformation in the closely packed solid state. It would also be interesting to discuss the variation of R_{CsCl} in solid solution with concentration and to compare it with the corresponding aqueous solution. It should be observed, however, that the errors involved in refractive index determination in our case are relatively large compared with the methods followed by the workers of the Fajans school and therefore no great claim is made about the absolute values of R . They can, however, be safely utilised for comparative purposes and are not to be confused with standard values.

It is to be expected from the Fajans theory that smaller the cation, for the same valency, the greater will be its deforming action on a particular anion with consequent lowering in the value of R for the salt. LiCl should therefore show the largest amount of divergence between R_{sol} and $R_{\text{cryst.}}$, the respective values being 8.76 and 7.59 c.c. What strikes us, however, is its extremely low value in solid solution, varying between 2.52 and 3.17 c.c. for the concentration range investigated. Such wide departure from the value in the crystal state and in solution in water may only be attributed to particularly strong deformation. This will not be explained by change of dielectric constant alone, although it undoubtedly plays an important role, as in the same medium CsCl shows but little divergence—a fact which can be easily explained on the basis of the Fajans theory. Hence the dielectric constant factor is not alone sufficient to explain the abnormal lowering in the value of mole refraction in the case of LiCl. It is, however, surprising

that the value can be lowered from 7.52 c.c. in the case of the crystal to 2.42 d.c. in solid solution. The concentration effect of LiCl in aqueous solution has not been unfortunately thoroughly studied in the past although the change of R for LiClO₄ for different concentrations is available (Geffcken, *Z. physikal. Chem.*, 1929, 8B, 113). The value of R in this case increases with concentration, which is also found to be the case with LiCl in the present case.

In the case of NaCl, the divergence of R from R_{cryst} is marked although not so great as in the case of LiCl. The maximum value 6.26 c.c. in our case may be compared with 8.50 c.c. for the pure crystal. The value of R , however, increases instead of decreasing with concentration as in the case of the aqueous solution, although the increase is less marked than in the case of the previous salt. The same phenomenon is noticed in the case of KCl, in which case also, R shows slight increase with concentration. But in both the cases, the respective values of R are decidedly smaller than R_{cryst} .

In the case of RbCl, the variation of R with concentration is much smaller and the order follows that for aqueous solution, although the individual values still show some amount of divergence.

The most interesting case is that of CsCl. Here although concentration has slight lowering effect as in the case of the aqueous solution but the values do not markedly differ from that of R_{cryst} . The minimum value in our case is found to be 14.99 as against 15.20 c.c. for crystal. This is a striking confirmation of the Fajans' rule even in solid solution.

The dielectric constant of B₂O₃ glass according to Thomas (*J. Phys. Chem.*, 1931, 35, 2109) has a value 3.5. The different alkali borates have values lying between 6.44 and 7.50 (Landolt Börnstein Tabellen, 1923, II, 1033), compared with water these values are remarkably small. It may be expected therefore that lower dielectric constant of the medium will cause a closer approach of the constituent ions of the crystal in solid solution causing a strong deformation. This would be a purely electrostatic effect. This effect will be more or less identical with different polar crystals of the type XCl in the same medium if dielectric constant alone were the deciding factor. The fact that LiCl is most strongly and CsCl very feebly deformed in the same medium lends strong support to the view that the small cation having a large surface density of charge strongly polarises the anion, while the comparatively large cation with a smaller surface density of charge brings about but little polarisation of the anion. Wulff and Majumdar (*loc. cit.*) investigating the system $x\text{Na}_2\text{O}$, $y\text{B}_2\text{O}_3$, arrived at a similar conclusion that Na₂B₄O₇ in solid solution in B₂O₃ is very strongly deformed and the deform-

ation produced is of a much higher order than in the crystal or in aqueous solution.

This means that LiCl exists in all probability in the associated (as opposed to ionised) state in solid solution of glass. The co-valent nature of the binding force progressively changes into electrovalent until CsCl is reached, in which even in the glass state, the constituents are most likely in the same condition as in the crystal.

The reason why the slope of the concentration-mole refraction curves show an opposite sign to those in the case of corresponding aqueous solutions may be explained as due to the mutual effect of the constituent ions of the electrolyte on the solvent medium.

Hence it can be asserted that the view point of Biltz that in every case the mole refraction of the constituents persists as additive functions when they go to form a glass system is untenable. This is only true in case of polar crystals having a comparatively large cation. Moreover, the polarising power of the cation for a particular anion follows the inequality :

$$\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs},$$

and this is fully consistent with the postulates of Fajans theory of deformation.

The lattice distances of the alkali halides in the same solvent have been measured by the Debye-Scherer method and certain interesting departures have been observed. This will form the subject matter of a future communication.

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART V. THE SOLVENT - SOLUTE RELATIONSHIP OF RESINS IN MIXED SOLVENTS.

BY SANTI RANJAN PALIT.

It has been found that if a resin is dissolved in a non-solvent by addition of a solubiliser, which itself may or may not be a solvent for the resin, the proportion of the solubiliser necessary to confer complete solubility is the less, the higher the proportion of resin to the non-solvent. This is supposed to be true for all lyophilic solutes. On ultimate analysis it transpires that the above behaviour of resins has some similarity with liquids in their behaviour towards organic solvents. The solubility curves are of the limited miscibility type for liquids but are highly unsymmetrical, and it is suggested that this is an intrinsic property of resins in particular and lyophilic solutes in general, and is caused by the capacity of resin molecules for immense solvation.

The concept of solubility as developed in the case of ordinary solutes is difficult of application to resins due to their peculiar behaviour towards solvents. If a purified resin is soluble in a solvent, say, rosin in alcohol or benzene, it is generally found to be soluble in that solvent in all proportions producing from jelly-like consistency to thin fluids depending on the concentration of the resin. This bare fact itself makes the idea of solubility and saturation superfluous. On the other hand, if a pure resin is found to be insoluble in a particular solvent, for example, pure shellac resin in benzene, or say, ester gum in alcohol, the maximum amount dissolved by the solvent is very small from about 1% down to practically zero concentration; of course, the resin generally swells or gels in contact with the non-solvent. Intermediate values of solubility of pure resin producing true saturation equilibrium are, however, very seldom met with. The enquiry naturally suggests itself about the cause of the existence of only such extreme solubilities.

The author has conceived the idea that in suitable mixtures of a solvent and a non-solvent or of two non-solvents having good solvent power, measurements of solubility might be possible and the results may throw light on the fundamental question of solvent-solute relationship for resins in particular and lyophilic solutes in general. The present paper describes the results of such investigations which bring forth very clearly the distinctive nature of resins in their role as solutes.

EXPERIMENTAL.

The study has firstly been made with a mixture of acetone and glycol, which is an excellent solvent for shellac, whereas the components are individually non-solvents. After some trials in different ways, the following method has been found suitable and has been used for the purpose.

In a number of stoppered sample tubes ($4'' \times \frac{7}{8}''$) definite quantities of dry finely powdered shellac were taken. To each were added from micro-burettes, calculated volumes (about 5 c.c.) of say, acetone, to bring the relative proportion of shellac to acetone to the same value in each of the tubes. Measured volumes of glycol were then added to each tube from microburettes so that its proportion varied by small steps (0.5% or less) from tube to tube. The tubes were regularly shaken in a thermostat (25°). It was observed that up to a particular percentage of glycol, complete dissolution of shellac took place, whereas the contents of those tubes, which were weaker in glycol, remained non-homogeneous even on keeping indefinitely. Similar experiments were also conducted, with different ratios of shellac to glycol by adding small quantities of acetone in small steps, to find out the solubility limit. That we are dealing with a real equilibrium has been tested and proved as follows. Any mixture, which just fails to produce complete solutions is made homogeneous by slight rise of temperature. On being replaced in the thermostat, non-homogeneity invariably appears in a short time, showing that a homogeneous phase is not possible under the given conditions. These experiments yield data on the minimum proportion of one of the solvents necessary to confer solubility to definite ratios of shellac to the other solvent.

In the graph, the line of gelation is also given which divides the gel region from the fluid region. The points on this line of gelation have been experimentally determined as follows. Gelation temperatures (as near as possible to 25°) were measured for two different concentrations of shellac in the same solvent mixture. The gelation concentration at 25° was found out by graphical extrapolation or interpolation of the straight line obtained by joining these two points. That such extrapolations are permitted over small range has been shown by the author in a gelation study of such systems (Part VI, p. 266).

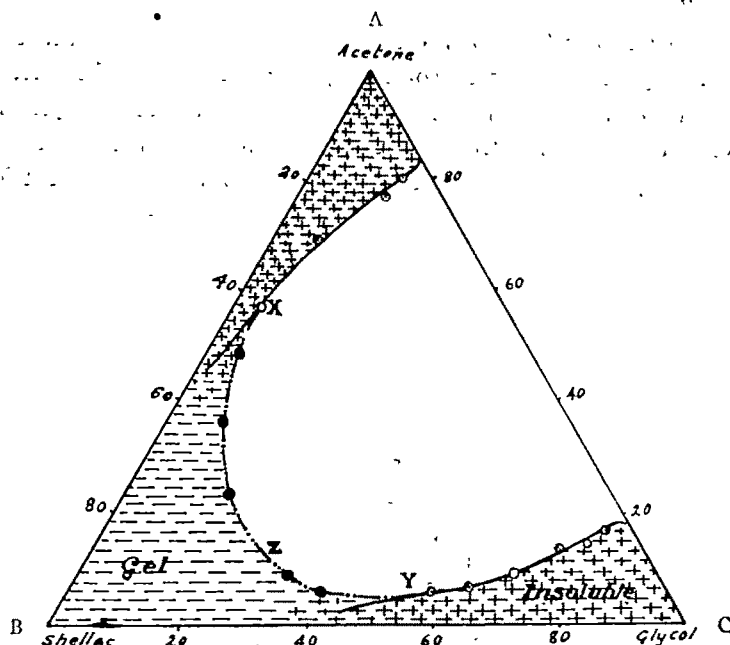
The experimentally obtained results are given in Table I and have been plotted on a three-component triangular diagram (Fig. 1).

TABLE I.

| Shellac: glycol (by wt.) | Acetone for complete soln. | Shellac: acetone (by wt.) | Glycol for complete soln. |
|-----------------------------|-------------------------------|------------------------------|------------------------------|
| 5:95 | 16.4% | 5:95 | 15.5% |
| 10:90 | 14.5 | 10:90 | 14.6 |
| 25:75 | 13.3 | 25:75 | 7.8 |
| 33.3:66.6 (1:2) | 9.1 | 40:60 | 5.9 |
| 40:60 | 6.5 | | |
| | 5.3 | | |

In the diagram, the blank portions indicate complete solubility, the lightly shaded portions (parallel broken lines) gels, and the deeply shaded portions (crossed lines) non-homogeneous mixtures. The variation of solubility

FIG. 1.



Mutual solubility relationship of shellac, acetone and ethyleneglycol

with composition of solvent is worth noticing. Taking this definite case, the amount of glycol necessary to make a homogeneous phase depends on the ratio of shellac to acetone and rapidly falls as the proportion of shellac increases. For example, for a 1:19 ratio of shellac to glycol, 16.4% of acetone are necessary, whereas, for a 1:2 ratio of the same, 6.5% acetone of

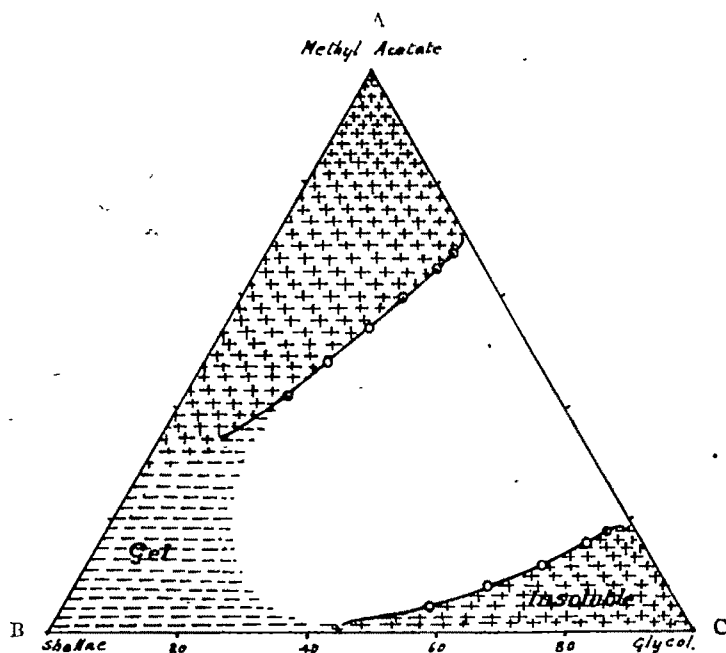
TABLE II.

| Shellac: glycol (by wt.). | Methyl acetate for solubilisation. | Shellac: methyl acetate (by wt.). | Glycol for solubilisation. |
|------------------------------|---------------------------------------|--------------------------------------|-------------------------------|
| 5:95 | 17.7% | 5:95 | 29.6% |
| 10:90 | 16.0 | 10:90 | 28.2 |
| 20:80 | 11.5 | 20:80 | 25.9 |
| 30:70 | 8.4 | 30:70 | 23.5 |
| 40:60 | 5.0 | 40:60 | 19.5 |
| | | 50:50 | 16.3 |

the total weight are required for complete solubility. This is also conversely true, i.e., for the amount of acetone necessary for making homogeneous any ratio of shellac to glycol. This tendency has already been observed to exist with water as 'solubiliser' for dissolving shellac in acetone (Palit, *J. Indian Chem. Soc.*, 1940, 17, 303).

If any substance (solute) is insoluble in any solvent, A, and if it can be made soluble by adding a second solvent B, the solvent B will be referred to in this paper either as solubiliser in conformity with our previous practice, or 'solutizer,' a term used in petroleum technology in a similar sense (*Chem. Met. Eng.*, 1940, 46, 776) irrespective of whether B itself is a solvent for the solute or not.

FIG. 2.



Mutual solubility relationship of shellac, methyl acetate and ethylene glycol.

Complete solubility diagram for another similar system, shellac in glycol-methyl acetate, has also been experimentally obtained. The experiments are comparatively easy and the data more accurate for this system, since it behaves in a peculiar way particularly at somewhat lower concentrations of shellac. On addition of shellac to a homogeneous mixture of methyl acetate and glycol, two immiscible liquid layers separate, the upper one being a solution of methyl acetate and glycol with a trace of shellac,

while the lower layer is a solution of all the three components. As the proportion of the solubiliser is increased, the upper layer decreases in volume until at a definite concentration it just vanishes. The data are presented in Table II and are graphically represented in Fig. 2. The general trend referred to is also very marked here; for example, for a 1:19 ratio of shellac to glycol, methyl acetate necessary is 17.7%, whereas for a 1:1.5 ratio of shellac to glycol, only 5% of methyl acetate suffice for complete solubilisation.

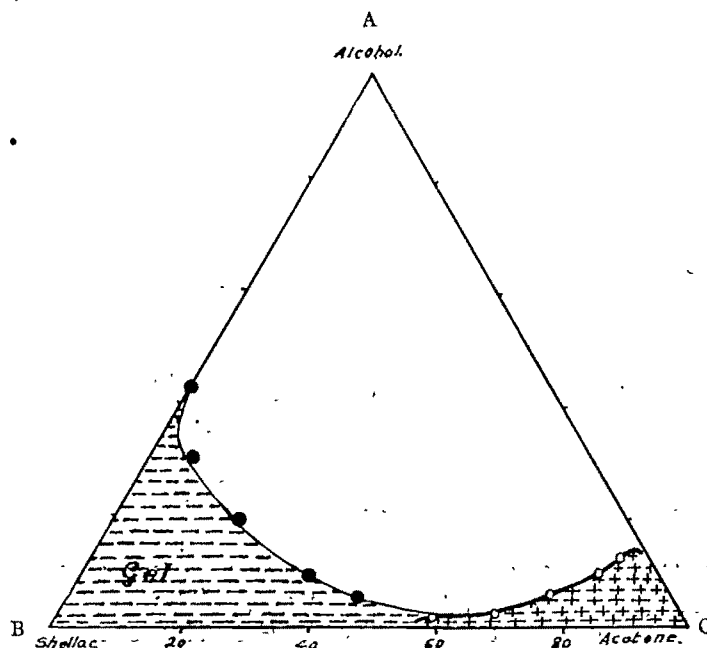
This same trend of the necessary proportion of the 'solutizer' to decrease steadily with increasing proportion of the solute, has been observed to be existing even when the solubiliser itself is a solvent so far as shellac-acetone solubilised by alcohol is concerned. The data for this system are presented in Table III and are graphically represented in Fig. 3.

TABLE III.

| | | | | | | | |
|--------------------------------|-----|------|------|-------|-------|-------|-------|
| Shellac: acetone | ... | ... | 5:95 | 10:90 | 20:80 | 30:70 | 40:60 |
| Alcohol for solubilisation (%) | .. | 12.4 | 9.6 | 5.8 | 2.3 | 1.7 | |

The existence of this tendency is evident from the graph. It should be pointed out that this behaviour would cease to exist

FIG. 3.

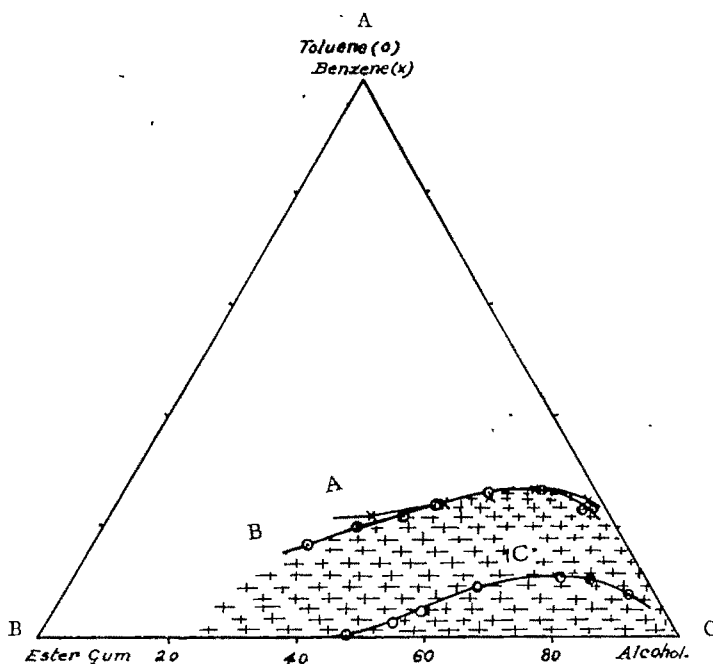


Mutual solubility relationship of shellac, acetone and alcohol.

for small concentrations of the solute, since the solubility curve should never meet the line, AC, as the solvents A and C are miscible in all proportions. The solubility lines should run very close to the line, AC, to meet the corresponding points, A₁ and C₁ (not shown in Fig. 3), which lie very close to A and C, and respectively represent the very small solubilities of the resin in the pure solvents. Hence the above mentioned trend would cease to exist and in fact, would reverse from some rather low concentration of the resin. Though this behaviour is not observable for shellac in the above curves, this is noticeable in the curves for ester gum in alcohol-toluene or benzene mixtures (Fig. 4).

Ester gum is the commercial name of the glycerol ester of rosin, which latter consists mainly of abietic acid ($C_{20}H_{30}O_2$ of M. W. 302). The gum (low acid value type) was purified by two extractions each time by keeping in contact with twice its own weight of alcohol for 24 hours with occasional kneading of the insoluble gummy mass. The gum was then dried in a vacuum oven at 70°, powdered and stored in vacuum desiccators.

FIG. 4.



Solubility curves of ester gum in benzene (or toluene)-alcohol mixture. The uppermost curve (points indicated by crosses) refers to benzene-alcohol and the next lower to toluene-alcohol mixture; the lowest curve refers to that of unpurified ester gum in toluene-alcohol mixture.)

Three solubility curves at 30° are shown in Fig. 4-'A' for benzene-alcohol mixture (indicated by crosses), 'B' for toluene-alcohol mixture and 'C' for the unpurified resin in toluene-alcohol mixture (the lowest curve, points indicated by circles). The points on the graph were experimentally determined not by the laborious method described for shellac, but by the less accurate precipitation method. The nature of the solubility curves is similar to the foregoing though the fall is rather steady and slow except in curve C. Also, the initial rise, which should be existing according to theory, is experimentally realisable and plainly observable in all the curves here.

The above mentioned behaviour appears *a priori* to be an intrinsic property for all highly lyophilic solute mixtures, and may be concisely expressed as follows :—

The amount of solubiliser which is just necessary for a lyophilic solute to make it completely soluble in any non-solvent (i.e., to produce a three component homogeneous system) decreases steadily with increase in the ratio of the lyophilic solute to the non-solvent after an initial steep rise at very low values of this ratio. This behaviour will be referred to later as the rule of resinous (or lyophilic) solubility.

Qualitative evidence for this rule of resinous solubility is perhaps experienced in any process of dissolving a resin in a mixture of two non-solvents, a striking case met with by the author is that of the synthetic resin, glyptal (low molecular weight type) which dissolves completely in a mixture of two non-solvents, *n*-butyl acetate and ethyl alcohol. The resin is soluble from about 15:85 to 65:35 alcohol-butyl acetate mixtures. It is observed that at any of these extreme compositions, if the solutions are strongly turbid due to the presence of insoluble resin, perfectly clear solutions can be produced by adding more resin. There is no doubt that these are cases of true equilibria since the turbid solutions are found to clarify on warming and again become turbid on cooling.

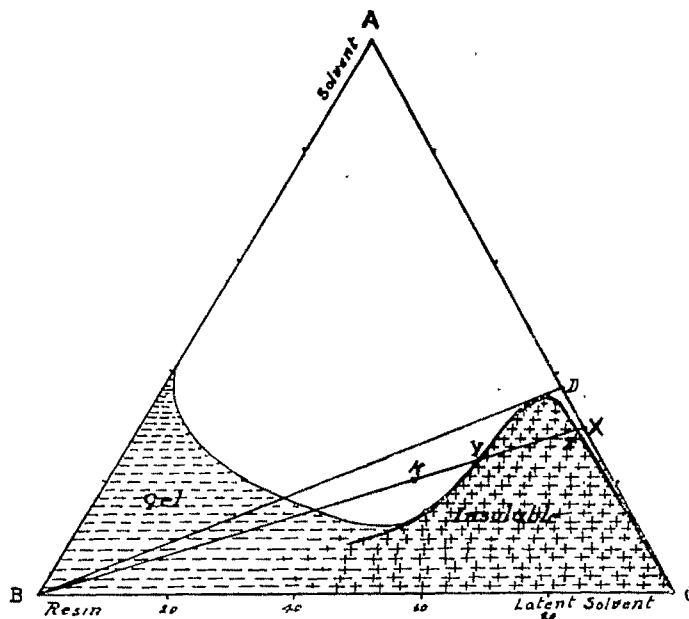
The rule of resinous solubility, as recorded in the paper, may be roughly explained if an assumption of strong solvation is made, different chemical groups being attracted to different parts of the molecule. We need further assume that the solvation of any part of the shellac molecule by any solubiliser molecule is a dynamic equilibrium, as pictured by Langmuir for adsorption of gases on surfaces of metals. When the proportion of shellac increases, the requisite proportion of the 'solubiliser' will be necessarily reduced, since the same solubiliser molecule due to a closer proximity of the solute molecules may do the duty for a number of them by fixing itself successively to each of them in such a small interval of time that the big

solute molecules have hardly time to unite to form flocks for precipitation. The reduction of the necessary solvation area by reversible association of the resin molecules to form not too large micelles, may be another contributing factor.

DISCUSSION.

The solubility curves for resins as presented above differ in some essential and fundamental respects from those for ordinary solid solutes. The curves for ordinary solutes in a mixture of two liquids may be of varied types and sometimes may show binodal behaviour (Taylor, "Physical Chemistry", Vol. I, p. 580). But whatever be the type of the curve, it always implies that at any particular composition of the solvent mixture, there is a maximum proportion of the solid which it can dissolve and beyond which it cannot.

FIG. 5.



Typical solubility curve of a resin in a solvent-latent solvent mixture.

On the other hand, from the diagram (Fig. 5), which represents a typical case of a resin satisfying the rule of lyophilic solubility, it is evident that for all mixtures of the solvents from pure A to a composition represented by the point, D, the resin is completely soluble in it in all proportions.

For all compositions between C and D, the resin is completely soluble only if it is present above a certain concentration. Thus, for example, for the solvent mixture, X, the resin must be present in a concentration higher than Y to form a homogeneous solution; if the concentration of the resin falls below Y, an insoluble phase will separate. Hence, we come to the fundamentally reverse fact that it is sometimes possible for a resin to be soluble in a solvent mixture, either to produce from cent per cent to zero per cent resin concentration or from cent per cent to a minimum value below which its concentration can never be reduced.

These solubility curves lead to another interesting conclusion. Suppose a solution of the composition, K, is prepared by dissolving sufficient quantity of the resin in the solvent mixture, X, and the solution is diluted by adding the same solvent mixture; precipitation of the resin should occur, since the line KX passes through the non-homogeneous region. It often happens that a resin may contain more than one component, or some impurities, one of which by itself may be capable of producing this type of solubility curve with a solvent, thus giving rise to such complicated solubility phenomena. Numerous examples may be cited. Commercial ester gum contains the resenes (hydrocarbons) as well as free abietic acid originally present in the rosin from which it is made. Hence, it is generally found to be perfectly soluble in alcohol in the ratio of about 55:45 or higher to produce a rather mobile solution, but this solution on dilution with alcohol separates a curdy white coagulum. The resene is here playing its role as the solubiliser for the true ester gum (abietic triglyceride) in alcohol. If, however, the hydrocarbon and other impurities are removed by repeated extraction with large volumes of alcohol, no such thing happens. Incidentally, this is the reason of the great difference between the solubility curves (Fig. 4, curves B and C) of the purified and the commercial ester gum in alcohol-toluene mixture. Kauri gum is another example. It is found completely soluble in ethyl acetate in the proportion 1 g. : 1.4 c.c., but the solution, on dilution with the same solvent, throws out a shining white coagulum, which on further washing with ethyl acetate becomes practically insoluble in it, and no longer shows such behaviour (for further examples of anomalous solubility and discussions *vide* Palit, *J. Indian Chem. Soc.*, 1940, 17, 308; Lange, "Handbook of Chemistry," 1937, p. 1035).

Comparison of Resins with Liquids.

Unlike crystalline solutes, liquids have got some degree of resemblance with resins in their behaviour towards solvents, the most striking of which

are—(i) separation into two liquid layers, (ii) mutual solubility phenomena, and (iii) similarity of solubility curves in mixed solvents.

(i) It frequently happens that if a small quantity of a resin be added to a solvent mixture, separation into two mobile liquid phases occurs. Two most striking cases observed by the author are shellac in methyl acetate-glycol and purified ester gum in xylene-alcohol mixture. The most convenient proportion for such observations at 25° is 30:70 glycol-methyl acetate to which is added shellac to about 15% of the total weight and 60:40 alcohol-xylene to which is added purified ester gum to about 30% of the total weight. This has apparently some similarity with adding, say, benzene or cyclohexane to a mixture of alcohol and water, when at some stage two liquid layers will separate. But unlike liquids, the two liquid layers tend to merge into one with higher concentration of the resin, often with the formation of a clear gel.

(ii) The equilibrium between a swelled resin and the swelling liquid is often regarded as [of the mutual solubility type, as observed with ether-water. Bronsted and Volqvartz support this view from a study the behaviour of 'eucolloidal polystyrenes against pure solvents and solvent mixtures (*Trans. Faraday Soc.*, 1939, **35**, 576; 1940, **36**, 619).

More definite proof, however, is available from a study of the precipitation temperature of resin solutions. Since the question of precipitation of resin is intimately bound with that of gelation, we shall present the results at length in our subsequent study on gelation of resins. A typical curve is, however, reproduced in Fig. 6, which is sufficient to prove our thesis. These were obtained by cooling resin solutions of definite concentrations and noting the temperature at which turbidity or haziness first appears. By suitable choice of solvent, the precipitation curve can be followed to a concentration of about 40% of resin without interference due to gelation. One striking and unexpected similarity with liquids is that except at very low concentration of the resin, this temperature of precipitation can be determined like liquids with precision and reproducibility since they are quite reversible and show no lag. This itself is a typical liquid-like behaviour since all solids show more or less a tendency towards supersaturation. The most notable feature of the curves is that the precipitation temperature, after perhaps an initial steep rise, falls steadily with increase in proportion of the resin; in other words, we have to cool a 20% resin solution more than a 10% resin solution in order to produce precipitation. This is exactly the reverse of what would happen for all typical solids and has similarity with partially miscible liquid pairs like ether-water, phenol-water etc. In one characteristic feature, these curves

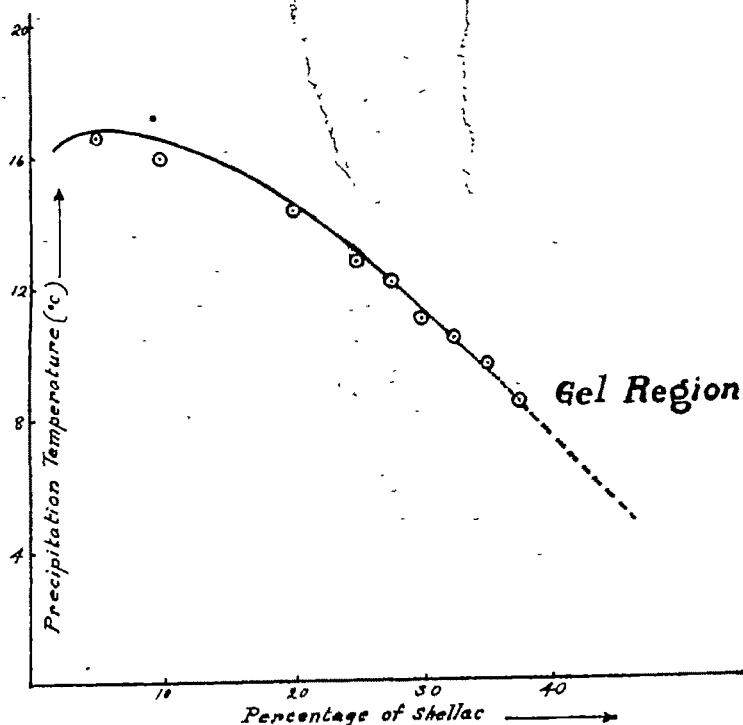
derivatives in various solvents (Berl and Koeber, *J. Amer. Chem. Soc.*, 1939, **61**, 154). It has, however, not been suspected that they are behaving like liquid pairs of limited miscibility.

The existing data are too scanty to examine how far this behaviour is typical of all lyophilic solutes. Larson and Greenberg, however, recorded an observation with gelatine in glacial acetic acid (*J. Amer. Chem. Soc.*, 1933, **55**, 2798) which clearly points to this type of mutual solubility. They observed that gelatine is soluble in glacial acetic acid only above a particular concentration, and non-homogeneity appears if the concentration of gelatine falls below this. The precipitation curve given by them have a striking resemblance with our precipitation curve (Fig. 6) and the observations become immediately understandable if the system is supposed to be of this type of lyophilic mutual solubility with highly unsymmetrical solubility curve.

Mardles' data (Alexander "Colloid Chemistry", Vol. IV, p. 95) on the precipitation temperature of cellulose acetate in benzyl alcohol and benzyl acetate only partially corroborate our view point as he finds that "For very dilute sols the temperature (of precipitation) rises with concentration, but eventually remains nearly the same over a wide range of concentration (beginning at about 2 to 5% as appears from his data) and then falls with further increase". It is, however, doubtful if with the old type high viscosity cellulose compounds, true equilibrium can ever be obtained. The author's experiments with low viscosity ethyl cellulose are interesting as it has been observed that similar to resins, higher concentrated solutions have lower precipitation temperatures, which are far widely separated, to be explicable from any other cause. Thus, the observed precipitation temperatures of 1%, 3% and 5% solutions in a 10:90 mixture of *cyclohexanol-cyclohexane* are 25.5°, 17.0° and 12.5° respectively which are reproducible to at least $\pm 1^\circ$.

(iii) The solubility curves of resins in a mixture of two liquids as observed in Fig 1 to Fig. 4 differ from similar curves for three liquids, for example, benzene, alcohol and water, in the aspect that for the latter the tips of the solubility curves are somewhere midway between the two sides and not very close to one side as in the case of resins. In Fig. 7, a number of such solubility curves are given, where curve I is the solubility curve of benzene (B) in a mixture of alcohol (solvent, A) and water (non-solvent, C). All these curves should necessarily show a maximum, since the solvents A and C are miscible in all proportions, but the maxima, D, generally lie midway between the sides, AB and AC and not close to AC as in the case of resins. We may hence, plainly state that

FIG. 6.

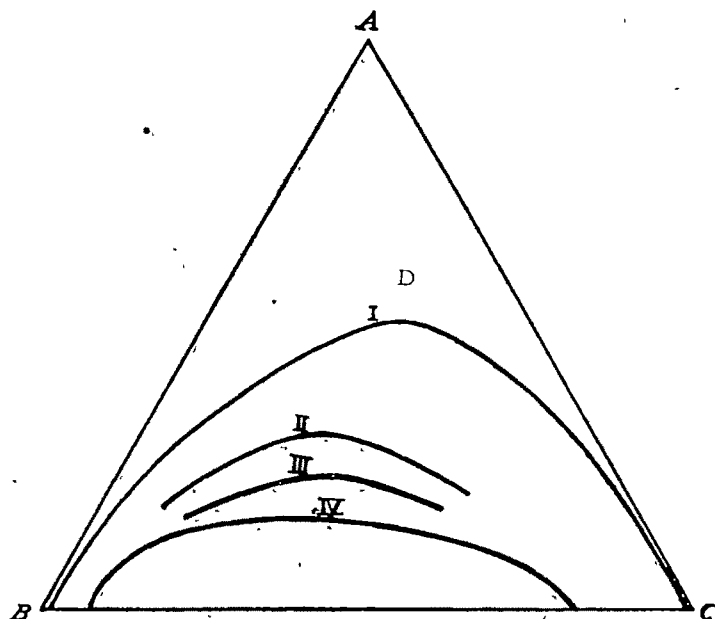


Precipitation curve of shellac.

for resins are differentiated from the latter types; unlike the latter, the curves are highly unsymmetrical, the tip of the curve being very close to the side opposite to that of the pure resin. Expressed explicitly *resins in their behaviour towards organic solvents behave like a partially miscible liquid pair with respect to upper critical solution temperature, which occurs with rather low concentration of the resin, thus giving the curve a highly unsymmetrical shape.* It is noteworthy that the view, that resins as vitreous bodies are supercooled liquids, is substantiated by a study of their solutions.

The observation of the existence of a lower critical solution temperature for a resin-solvent system will be nothing unexpected as some molecular colloids are known to exhibit such behaviour. Thus, nitrocellulose has been found to be soluble in alcohol at liquid air temperature but not at ordinary temperature (McBain, Harvey and Smity, *J. Phys. Chem.*, 1926, 30, 347), methylcellulose in water at lower temperature but not at higher (Heymann, *Trans. Faraday Soc.*, 1935, 31, 846), and some cellulose

FIG. 7.



Solubility diagram of ternary liquid mixtures.

resins have a close similarity with liquids, with the distinction that due to some inherent characteristic, the maximum point D lies close to the side, AC i.e., they behave like liquids with highly unsymmetrical solubility curve. This inherent nature is most probably constituted by the capacity of the resin molecules for immense solvation.

The same remark is also applicable in a comparison of the case of a resin dissolving in a mixture of two non-solvents with that of a liquid of limited miscibility with it except that here we have to deal with two binodal curves instead of a single curve. This definitely shows how the resins are basically differentiated in their behaviour from solids and liquids with some qualitative resemblance with the latter.

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART VI. ON THE RELATIONSHIP BETWEEN PRECIPITATION AND GELATION OF RESINS.

BY SANTI RANJAN PALIT.

Precipitation and gelation curves of de-waxed shellac in a solvent mixture of acetone containing 10% by weight of glycol were determined with a view to elucidating the mechanism of the formation of varnish films in which gel-formation plays an important role.

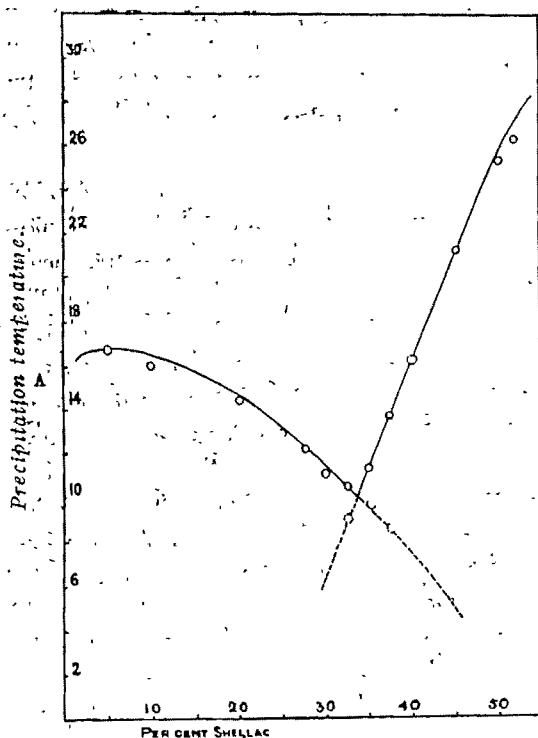
It is an established fact that a sol forms a thermo-reversible gel on cooling, only when the concentration of the lyophilic solute is above a minimum (Freundlich, "Colloid and Capillary Chemistry", 1926, p, 700; Mardles, *Trans. Faraday Soc*, 1923, **19**, 118). If the concentration of the solute is below this minimum, precipitation of a portion of the dispersed phase occurs. The gelation temperature (i.e. sol-gel transformation point) *versus* concentration curves have been determined for many lyophilic substances, but it has so far not been possible to determine their precipitation curve (which is of course identically the same as the solubility curve) below minimum gelation concentration. This lack of data is ascribed to two reasons. Firstly, the minimum gelation concentration is very small for most substances and hence investigation into this region is very difficult. Secondly, even if it were possible to investigate such low concentrations, which will necessarily have inconveniently low precipitation temperatures, reliable data would hardly be obtained due to supercooling, interferences from the colloidal nature of the solute and other disturbing factors.

Natural resins and synthetic resins of low molecular weight do not offer any of the above difficulties. Their minimum gelation concentrations generally lie between 25 and 44% concentration of the resin and secondly, their precipitation temperature can be determined with great accuracy, since a number of them have been observed (Palit, *J. Indian Chem. Soc.*, 1942, **19**, 253) to behave in solution more like partially miscible binary or ternary systems than like ordinary solid solutes. Hence, here is a chance of determining the precipitation and the gelation curve of the same substance in the same solvent, and the present communication describes results of investigations with this object in view. Although the results obtained are of a preliminary nature, they are considered sufficiently important to be worthy of record at this initial stage, since the results can throw much light on some vexed questions about gelation. The work is, however, being followed up to elucidate the mechanism of varnish film formation during which gel formation plays an important role.

As the resin, shellac has been chosen for study. The proper choice of solvents is an essential pre-requisite to success in such experiments. For

example, if alcohol is used for such determination with shellac, the gelation and precipitation temperatures are too low at small concentrations to be experimentally determined.

FIG. 1.



Intersection point of the curves represents 'C'. . . graphically in Fig. 1.

The experiments have been conducted with de-waxed shellac as the resin, and acetone containing 10% by weight of glycol as the solvent mixture. This composition of the solvent mixture has been chosen after much preliminary experiments with various combinations, since this composition produces precipitation and gelation in a very conveniently workable temperature range. The precipitation and gelation points have been determined by very simple methods of gradually cooling the solutions contained in thin test tubes. Precipitation point is determined by noting the temperature at which opalescence starts. The temperature at which, in about 10 minutes, the liquid ceases to flow on inversion of the test tube is taken as the gelation point.

Before discussing about the curves, it should be mentioned, as explained in a previous paper (Palit, *loc. cit.*), that the precipitation temperature can be

All ordinary common solvents for shellac were found to be too good solvents to be employed in such experiments. Hence, the author has been forced to use a mixture of solvents, which would give precipitation and gelation in the easily measurable region of temperature scale. Of course, there is absolutely no reason, why such a suitable resin-pure solvent system should not exist, but failing to discover such a type of combination as meets our requirement, the author has resorted to the next best, i.e. a suitable mixture of solvents. The experimental results are shown

determined very precisely to an accuracy of 0.1° , more precisely towards the rapidly falling portion of the curve BC (curve on the left). The gelation temperature can be reproduced to an accuracy of 0.2 , and the difference between gelation temperature and the melting point of the gel, unlike all other jellies, is very small, seldom exceeding 0.4° . A relieving feature of these experiments is that the gelation temperature is free from any appreciable lag, i.e., it is practically independent of the rate of cooling. The data for very low concentrations of shellac (portion AB) are much less accurate than indicated above due to the difficulty of noting the exact beginning of precipitation, and due to a comparative lack of the high degree of reversibility which exists for higher concentrations (portion BC).

The curves ACD are self-explanatory: the portion AC is the precipitation curve; whereas CD (curve on the right) is the gelation curve. The most characteristic and unexpected feature of the precipitation curve is that leaving out a small initial portion of the curve, the solutions become thermally stabler, the higher the concentration of the solute; in other words, a solution which contains 30% shellac requires more cooling for precipitation than a solution of 20% strength. The gelation curve, however, has the usual feature of having a higher gelation temperature for higher concentration of shellac. The dotted portions are actually realisable by suitable adjustments of experimental conditions, as is to be shortly explained. The first unstable point, (indicated by dotted circles) as occurring with at 32.5% shellac solution, indicates that if such a solution is slowly cooled below 10.4° , the whole thing becomes turbid due to precipitation of a new phase. But, if, on the other hand, it is very rapidly cooled below 9° , a slightly hazy elastic gel forms, which slowly becomes turbid due to precipitation of the resin. The first distinctly visible insoluble mass separates in about 5 to 10 minutes. The next unstable point corresponding to a concentration of 35% shellac is of a slightly different significance. On cooling such a solution it becomes an elastic non-flowing gel at 11.2° . On further cooling, nothing happens until the temperature goes below 9.6° , when the gel becomes turbid due to copious precipitation. In fact, the gel was kept for 5 hours between 9.8° and 10° without the slightest opalescence occurring, whereas at 9.2° copious precipitation occurred in 15 minutes. The third and the other unstable points have similar significance, except that it takes more time for precipitation to start as the solution gets more and more concentrated. For a 50% solution, gelation occurs at 25.2° , whereas precipitation could not be induced on keeping at 0° for 24 hours, though the extrapolated precipitation temperature from the curve would be at about 2° .

The outstanding feature of the curves is that they divide the whole region into four parts and clearly sets forth the condition under which

a gel should be stable or unstable. But whatever may be the type of gel, the results clearly establish that the precipitation curve is quite distinct and separate from the gelation curve. It has been upheld in some quarters (Von Weimarn, Alexander's "Colloid Chemistry," Vol. I, p. 81; Lloyd, *ibid.*, p. 777; Weimarn and Hagiwara, *Koll.-Chem. Beih.*, 1927, **23**, 400) that gelation is a limiting case of precipitation and Bradford (*Biochem. J.*, 1918, **12**, 351; 1920, **14**, 29, 74) goes so far as to suppose that the precipitate is crystalline. If it is so, the precipitation curve and gelation curve should be a continuation of each other. The results obtained in these experiments not only discredit such a theory, but explicitly show that a resin gel does not differ from the solution, from which it is derived by cooling, in so far as its property to precipitate a new phase is concerned, since both are given by the same precipitation curve. We have shown in a previous publication (Palit, *loc. cit.*), that a resin-solvent system is a mutual true solution, which is undoubtedly non-colloidal at least when dilute and hence, a resin gel is to be regarded as a mutual true solution of the resin and the solvent which has attained such a high viscosity as to lose its property to flow. That during transition from a viscous sol to an elastic gel, no abrupt change in properties occur (Laing and McBain, *J. Chem. Soc.*, 1920, **117**, 1506; Brouse, *Ind. Eng. Chem.*, 1929, **21**, 242) is also known for soap and casein.

In the case of resin gels, we have thus been forced to depart from the usually accepted diphasic structure of gels. Of course, Procter, Katz and others, long ago, were inclined to view the protein gels as homogeneous systems (Procter, *J. Chem. Soc.*, 1914, **105**, 313; Procter and Wilson, *ibid.*, 1916, **109**, 307; Katz, *Koll.-Chem. Beih.*, 1917, **9**, 1; *Trans. Faraday Soc.*, 1933, **29**, 279), and Fischer (Fischer and Hooker, "Lyophilic Colloids", 1933, p. 3; *Kolloid Z.*, 1930, **51**, 39) in a series of papers attempted to bring forward evidences for his theory of 'inverse solution' for gels. It should be noted that these resin solutions and also many other systems are true molecular solutions and they are capable of forming reversible optically clear gels. Before advancing a colloidal theory for such gels, it is yet to be proved that reversible micellar aggregation takes place. On the other hand, unless the present state of knowledge on solvation (for a discussion *vide* Heymann, *Trans. Faraday Soc.*, 1935, **31**, 846; 1938, **34**, 689) is improved, it is useless to attempt to show how such immobilisation can be effected by solvation alone.

We have now to explain why shellac gels are so reversible in character, whilst most lyophilic gels show pronounced lag and hysteresis. Thus the setting and melting points of an agar gel may differ by as much as 60°, while

a difference of 5° or 10° is very common. This difference in character is manifest even in the viscosity behaviour of these gels. Whereas a shellac gel regains its original viscosity on melting within the short time by which temperature equilibrium is established (Palit, *J. Indian Chem. Soc.*, 1940, 17, 308), most lyophilic gels show considerable hysteresis. The explanation certainly lies in the nature of solvation of the unit in solution. It is probable that solvation itself is reversible for shellac due to its small molecule of rather not complicated shape being the ultimate unit in solution, while for the lyophilic colloids, the ultimate unit being either the micelle or the molecule of giant size, the adsorption of solvent is much less reversible. This can be more easily understood when it is recognised, as pointed out by Ostwald (*Kolloid Z.*, 1928, 46, 248) and by Haller (*ibid.*, 1929, 49, 47; 1931, 56, 257), that solvent molecules may remain held up even in absence of adsorption forces, in the various pockets and channels formed inside the micelle or inside the too big molecule due to its peculiar geometrical shape.

The data being very meagre, to explore further the various theoretical possibilities and inferences will be immature until further work is done in this field. Such a work is in progress. It may be pointed out here how this curve affords explanation of some observations with gels. In attempting to apply these results to other systems, we have to note that the solubility curve for other substances need not be of the shape observed for shellac and may not have the same degree of reversibility, whereas the gelation line will be more or less of this type for most substances except perhaps the inverse gel-forming ones (*e.g.* methylcellulose in water). Various possibilities may then occur for the ways in which the precipitation curve and the gelation curve would intersect each other giving rise to various types of peculiar phenomena. The more the solubility line tends to assume the usual shape, the more the region of unstable gelation would expand, and at times, this may come down to ordinary temperature. This is perhaps the reason why transparent gels of many substances, *e.g.*, dibenzoyl *l*-cystine, barium malonate, salts of organic acids, etc. have so strong tendency to separate amorphous or crystalline precipitate on keeping.

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STUDIES IN THE DISSOLUTION OF SOAPS IN MIXED SOLVENTS.

BY SANTI RANJAN PALIT.

Alkali metal salts of long-chain fatty acids show pronounced enhanced solvency in a mixture of solvents composed of a polyhydric alcohol, a monohydric alcohol or/and a hydrocarbon or a chlorinated hydrocarbon. Solubility data in various such binary mixtures have been presented, and a discussion of their relative solvent powers has been made.

An explanation of such mix-solvency based on solvation of the different parts of the molecule through Van der Waals' forces and hydrogen bridge formation has been offered. Experimental evidences to support this theory have been presented.

The necessary conditions for a solvent or mixture to be powerful for soap dissolution has been found out to be the presence of two adjacent hydroxyl groups and a hydrocarbon dissolving portion.

It has often been observed that a mixture of two non-solvents has a strong dissolving power for a substance, whereas the individual solvents are practically non-solvents for the same. As an abbreviation of this type of 'enhanced solvency in a mixture of solvents of very poor individual solvent power' we shall hereafter use the term 'mix-solvency' and such mixtures of complementary solvents as 'mix-solvents'.

The solutes, with which such mix-solvency occurs, generally belong to the class of compounds of high molecular weight *e.g.* proteins, cellulose derivatives, resins etc., the most well known example being that of nitro-cellulose dissolving in a mixture of alcohol and ether to form the familiar 'collodion'. Mardles (*J. Chem. Soc.*, 1924, **125**, 2244) has listed some typical examples and Sutermeister (Sutermeister and Browne, "Casein and its Industrial Applications", 1939, 2nd Ed., p. 73) illustrates this with casein. Mellan ("Industrial Solvents", 1939) records a good many examples of mix-solvency with various resins and cellulose derivatives; Meyer (*vide* Discussions on Staudinger's paper, Faraday Society Discussion on Polymerisation and Condensation, 1935, p. 334) also mentions a case of mix-solvency with rubber in so far that the portion of rubber insoluble in benzene can be made soluble by the addition of a small quantity of butyl alcohol. A few striking cases of mix-solvency with pure resin of shellac by the author have been observed (*J. Indian Chem. Soc.*, 1940, **17**, 300).

The theory of the process of mix-solvency is, however, little understood though various explanations have been offered from time to time based on the assumption of dissociation of the solvent (*cf.* Byron

J. Phys. Chem., 1926, **30**, 1116), association of the solvent (*cf.* Barr and Bircumshaw, *Trans. Faraday Soc.*, 1921, **16**, 99), polar and non-polar adsorption (*cf.* Esseln, *Ind. Eng. Chem.*, 1929, **12**, 801; Bogue, "Theory and Applications of Colloidal Behaviour", 1924, p. 645; Highfield, *Trans. Faraday Soc.*, 1926, **22**, 37), solvation of varied groups (*cf.* McBain Harvey and Smith, *J. Phys. Chem.*, 1926, **30**, 239, 312; Mardles *J. Soc. Chem. Ind.*, 1923, **42**, 127T, 207T), etc. It appears, however, that so far all studies in mix-solvency have been mostly qualitative in character and have been necessarily limited to amorphous, ill-defined or giant molecular compounds and a great advance of knowledge is expected if quantitative mix-solvency studies could be made with well defined chemical compounds of comparatively low molecular weight. Since such dissolutions are generally associated with swelling, solvation, gel-formation, etc., such a study will be of paramount importance towards a general understanding of the relationship between the lyophilic solutes and their solvents. The author's finding (Palit, *Current Sci.*, 1941, **10**, 436) that alkali metal soaps show pronounced mix-solvency in suitable mixtures, has made such a study possible and the present paper records the first portion of the results obtained in this connection.

The author has observed that A-G-H mixtures (alcohol-glycol-hydrocarbon) are very powerful mix-solvents for alkali metal salts of long-chain fatty acids (sodium stearate, potassium palmitate, sodium oleate etc.), and A-G mixtures (alcohol-glycol) also exhibit this effect to a considerable extent. Quantitative data for such solubilities in mix-solvents will be presented herein and a theory of the process of mix-dissolution of soaps will be developed. Besides the evident theoretical interest, this study promises to be of great importance and usefulness in all industries which employ soap in organic solvents, and a discussion of these industrial aspects will form a separate communication.

EXPERIMENTAL.

Sodium stearate has been chosen as the representative member of soaps for study, a Merck's powdered pure variety, dried at 105-110° for four hours prior to use, being employed. The solvents are from various sources as recorded in the following list:—methyl alcohol (Merck's absolute, acetone free), ethyl alcohol (Merck's absolute), *n*-propyl alcohol (Schering-Kahlbaum), isopropyl alcohol (Alembic, India, pure), *n*-butyl alcohol (Merck, purified), isobutyl alcohol (B.D.H., Lab. reagent), isoamyl alcohol (Schering-Kahlbaum), acetone (Merck's analytical reagent), chloroform (Hopkin and Williams, Analar), ethyleneglycol (B.D.H. and Merck),

propyleneglycol (supplied by Griffin and Tatlock), diethyleneglycol (Boake Roberts & Co.), trimethyleneglycol (B.D.H. Lab. reagent), glycerol (Merck, bidistilled), α -chlorohydrin and β -chlorohydrin (B.D.H.). All the solvents in the above list appearing before ethyleneglycol, except the 'analytical reagents', were properly dried with freshly ignited Merck's pure calcium oxide and fractionated before use. The glycols were all twice distilled and the fraction boiling within two degree range in the second distillation collected. The chlorohydrins were distilled under vacuum and the products were quite neutral.

For solubility determinations, 2 g. of the stearate were taken in small stoppered conical flasks and were treated with 10 to 15 g. of the solvent mixture, delivered separately from microburettes correct to 0.02 c.c. from calculations of their densities. In experiments using glycerol, the proportions of the solvents were ascertained by actual weighing. The whole was left overnight to swell in an air thermostat (at approx. 25°) and placed next day in a thermostat (25° \pm 0.02°) for minimum four hours with periodic shaking. The contents were then poured into a fritted glass crucible filter in an air thermostat at 25° and pressure applied from above through a tightly fitted rubber stopper by compressed air. The whole filtration process took 20 to 40 seconds. The filtrate was collected in a solubility bottle placed in an almost closed space, saturated with the vapour of the volatile solvent, and after weighing was analysed for sodium stearate as follows.

0.2N-Alcoholic hydrochloric acid (10-20 c.c.) was added to the soap solution and then 10 c.c. of 'analytical reagent' chloroform to prevent the formation of fine colloidal dispersion of stearic acid during subsequent dilution with water. About 250 c.c. of water were slowly added when a heavy chloroform layer separated. The clear supernatant liquid and three washings of the chloroform layer, each time with about 30 c.c. water, were collected through a rapid filter paper and the filtrate was titrated against 0.2N-KOH. The method has been tested and found to give reproducible results with known weights (0.5-1.0 g.) of pure sodium stearate to an accuracy of about 2%. Of course, when the amount of sodium stearate in solution is small, the accuracy is comparatively small, since the method employs the difference between two titrations. The values of solubility thus obtained, in the case of pure alcohols, have checked well in all cases with the values obtained by a direct evaporation to dryness of known weights of alcoholic solutions.

Since these experiments are mainly designed to demonstrate in a quasi-quantitative and not too precise manner, the profound mix-solvency

with soaps, the order of accuracy attained in the present method seems sufficient for the purpose. The results have been expressed in weights of sodium stearate dissolved per 100 g. of the solvent. If 0.1 c.c. is the accuracy in the differential titration, and since 8 g. of filtrate are generally used for analysis, the accuracy in the final result comes to 0.07%, i.e. better than one in the first place of decimal. The accuracy could obviously be improved by using larger volumes of solvents but the war-time economy and restricted availability of solvents have stood against such a procedure. Another source of error is constituted by the removal of some solvents from the liquid phase through adsorption by the insoluble excess solid. This, perhaps, does not vitiate the result too much and can be counteracted by using just the least excess of the solid solute.

RESULTS.

The values of solubilities of sodium stearate in alcohol-ethyleneglycol mixtures are summarised in Table I and graphically represented in Fig. 1. The curves strikingly show the effect of mixtures in bringing about the dissolution; for example, while pure butyl alcohol dissolves 0.4%, and pure ethyleneglycol 1.3%, a mixture of them in the proportion 45:55 dissolves about 9% sodium stearate.

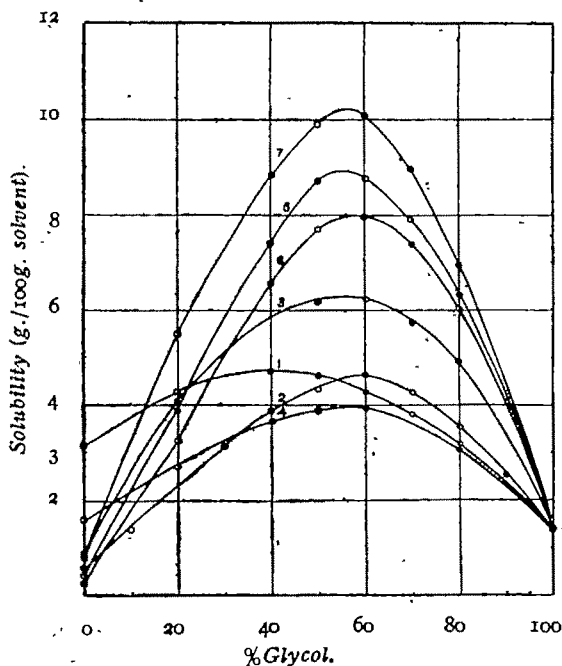
TABLE I.

Solubility of sodium stearate at 25°.

[illegible]

The chief feature of these curves is that all the curves show maximum, both sides of the maximum being more or less convex towards the horizontal axis, and in most cases the convexity of the right-hand side (*i.e.* nearer glycol) is more than that of the left-hand side. With the exception of methyl alcohol, all the maxima are in the region of 55 to 60% weight of ethyleneglycol. These values of maximum mix-solubility (S) are summarised in column 2 of Table II, and the optimum compositions, *i.e.* producing maximum solubility, appear in column 3 of the same table. It is evident from Table II and curves, that this maximum value of solubility for any combination of alcohol and glycol increases with increase in molecular weight of the alcohol used. Methyl alcohol is, of course, an exception to the above general trend, which may not be regarded as quite unexpected in view of its being the first member of a homologous series.

FIG. 1.



In order to compare the efficiencies of different mix-solvents, the ordinate of the maximum point cannot suffice, since it bears no relationship with the nature of the whole curve and the solubilities in individual solvents. Hence, a new term, the mix-solvency factor is introduced. This is defined as the ratio of the total area under the curve to the area under the straight line obtained by joining the two points representing the solubilities in the pure

solvents; in other words, it is the ratio of the average solubility over the whole mix-solvency curve to the mean value of the solubilities in the individual pure solvents. The calculated values of average solubility and mix-solvency factor for these different combinations are given in columns 4 and 6 respectively of Table II.

TABLE II.

Mix-solvency factor of glycol-alcohol mixtures.

| Composition of mix-solvents. | Max. solubility (S) | Opt. comp. Glycol : alcohol | Solubility Average (s). | Mix-solvency factor | |
|---------------------------------------|---------------------|-----------------------------|-------------------------|-----------------------------|---------------------|
| | | | | $s_m = \frac{s_1 + s_2}{2}$ | $f = \frac{s}{s_m}$ |
| Ethylene-glycol : MeOH | 4.72 | 40:60 | 3.75 | 2.24 | 1.67 |
| „ : ethyl alcohol. | 4.62 | 60:40 | 3.00 | 0.97 | 3.09 |
| „ : <i>n</i> -propyl „ | 6.27 | 55:45 | 4.37 | 1.11 | 3.94 |
| „ : <i>isopropyl</i> „ | 3.95 | 57:43 | 2.95 | 1.46 | 2.02 |
| „ : <i>n</i> -butyl „ | 8.94 | 55:45 | 5.48 | 0.88 | 6.23 |
| „ : <i>isobutyl</i> „ | 7.95 | 58:42 | 4.94 | 0.79 | 6.25 |
| „ : <i>isoamyl</i> „ | 10.20 | 56:44 | 6.52 | 1.10 | 5.93 |
| Diethylene-glycol : <i>n</i> -butyl „ | 4.77 | 52:48 | 3.17 | 0.75 | 4.23 |
| Propylene-glycol : „ | 4.85 | 62:38 | 3.32 | 1.34 | 2.48 |
| Trimethylene-glycol : „ | 1.16 | 50:50 | 0.88 | 0.54 | 1.63 |
| Glycerol : „ „ | 11.42 | 56:44 | 7.11 | 0.35 | 20.3 |

Before discussing mix-solvency, a very peculiar fact about the solubility of sodium stearate in pure alcohols may be pointed out. The value of sodium stearate increases and decreases alternately from member to member of the homologous series of alcohols up to amyl alcohol. The alcohols with an odd number of carbon atoms show much higher values of solubility than their neighbouring alcohols with an even number of carbon atoms. Thus, in methyl, propyl and amyl alcohols, due perhaps to some steric factor, the even-numbered members are unable to solvate the soap molecule as efficiently as the odd-numbered ones. In this connection, it is relevant to point out (*cf.* Bhatnagar and Prasad, *Kolloid Z.*, 1924, **34**, 194) that the electrical conductivities of stearates, palmitates and oleates of

sodium and potassium in propyl alcohol at equivalent dilution are much higher than the values in ethyl and butyl alcohol. Fischer (*Koll.-Chem. Beih.*, 1922, **15**, 1ff), however, found that with the exception of methyl alcohol, the gel-forming capacities of different alcohols for the same soap vary regularly from member to member of a homologous series. This may be taken as indicative of the fact that the factors which bring about gelation are not probably the same as those responsible for dissolution, a conclusion same as that reached by the author (forthcoming publication) from gelation studies of resins.

It should be kept in view when studying Table II that the values of maximum mix-solubility (S) and average mix-solubility (s) are much less liable to experimental error than the value of mix-solvency factor, (f), since the latter is a ratio, the denominator of which is comparatively small and subject to a large percentage error. Therefore, in comparing efficiencies between two mixtures of nearly equal mix-solvency factor, we shall consider S and s values rather than the factor, f , as indicative of their solvent power. A study of Table II leads to the following conclusions about mix-solvency. The power of producing mix-solvency effect increases with increase in molecular weight of the alcohol. For the same series of alcohol, the primary alcohol is far more powerful than the secondary one (compare data for propyl and isopropyl alcohols) and for the same primary alcohols, the straight-chained one is more powerful than the branch-chained ones (compare values of S and s for *n*-butyl and isobutyl alcohols). A striking and unexpected fact is that for the same glycol and different alcohols, the compositions of the solvent, which produce maximum solubility, are approximately at the same weight per cent of glycol, whereas for the same alcohol and different glycols, the maximum points do not crowd together so closely. These curves also furnish evidence against the assumption sometimes put forward without adequate experimental support that the optimum solvent composition, which is here the same as the composition producing maximum solubility, contains a definite simple molecular ratio of the two latent solvents. The optimum compositions, however, for all combinations containing glycol and alcohol (except *n*-butyl alcohol-diethylene-glycol) contain an excess of glycol by weight.

We have observed the variation of mix-solvency for the same glycol and different alcohols. It is of interest to study mix-solvency for the same alcohol and different glycols. In Table III are collected such solubility values, using *n*-butyl alcohol and four different glycols, ethylene, propylene, diethylene and trimethylene glycols and also glycerol; data on mix-solvency factor, etc. for these combinations are summarised in Table II.

Since glycerol, and probably any polyhydric alcohol resemble glycol in producing mix-solvency, the remarks made about glycols in this paper should be taken as applicable also to glycerol. In order to facilitate later discussions, the structures of the different glycols are also shown below.

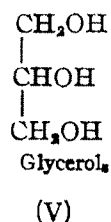
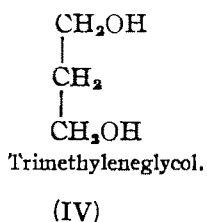
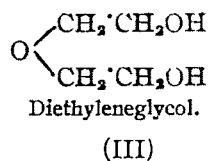
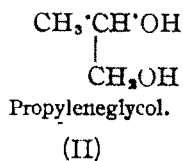
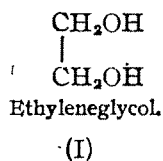


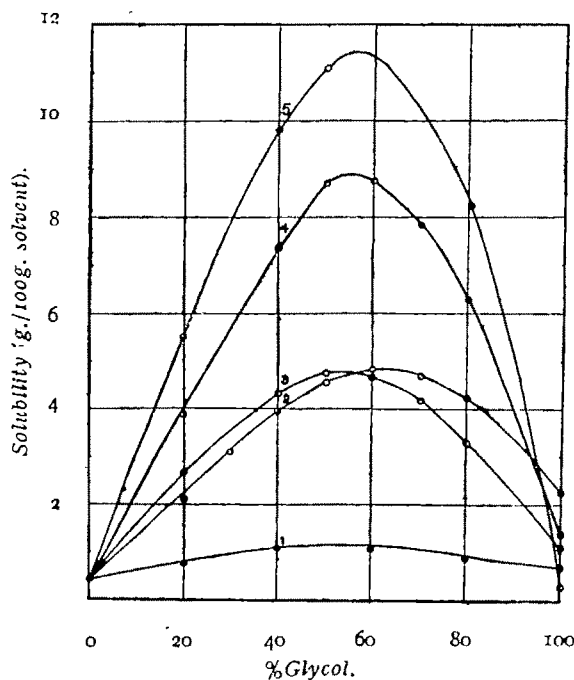
TABLE III.

Solubility of sodium stearate in n-butyl alcohol-glycol at 25°.

| <i>n</i> -Butyl alcohol :glycol (by wt). | Solubility (g./100 g.) in mixture of <i>n</i> -butyl alcohol and | | | | |
|--|--|-----------------------|------------------------|--------------------------|----------|
| | Ethylene- glycol. | Propylene- glycol. | Diethylene- glycol. | Trimethylene- glycol. | Glyciol. |
| 100 : 0 | 0.40 | 0.40 | 0.40 | 0.40 | 0.40 |
| 80 : 20 | 3.86 | 2.08 | 2.66 | 0.76 | 5.51 |
| 70 : 30 | — | 3.11 | — | — | — |
| 60 : 40 | 7.37 | 3.96 | 4.32 | 1.09 | 9.83 |
| 50 : 50 | 8.69 | 4.59 | 4.75 | — | 11.06 |
| 40 : 60 | 8.73 | 4.84 | 4.66 | 1.08 | 11.25 |
| 30 : 70 | 7.86 | 4.67 | 4.20 | — | — |
| 20 : 80 | 6.30 | 4.24 | 3.29 | 0.89 | 7.78 |
| 0 : 100 | 1.36 | 2.29 | 1.10 | 0.69 | 0.30 |

The mix-solvency curves (Fig. 2) are of the same general shape as the previous ones. In mixture with *n*-butyl alcohol, glycerol is the most powerful among this lot, considered from all aspects of mix-solvency. Of

FIG. 2.

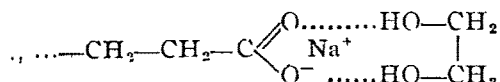


course, it is not certain, if the same order of efficiencies will be maintained with respect to any other alcohol. Among the glycols, ethyleneglycol is the most powerful latent solvent, both with respect to the values of maximum mix-solubility (s) and the mix-solvency factor (f). Propyleneglycol comes next, followed closely by diethyleneglycol with respect to the maximum (S) and average (s) mix-solubility, whereas the order is reversed with respect to the mix-solvency factor. Trimethyleneglycol produces very little perceptible mix-solvency. This fact is noteworthy showing the striking difference in mix-solvency effect between the two isomers, trimethyleneglycol (IV) and propyleneglycol (II), the two differing only in the relative position of the hydroxyl groups. Hence, a proximity of the two hydroxyl groups is indicated to be necessary.

DISCUSSION.

It is felt desirable to discuss this process of mix-solvency in the light of current ideas. The picture to follow is based on the ideas and considerations of various authors (McBain, *loc. cit.*; Whitby, *Colloid Symposium Monograph*, 1926, 4, 203; Meyer and Mark, "Der Anfeau der hochpolymeren organischen Naturstoffe", 1930, Chap. X; *Ber.*, 1931, 64B, 2913) about the process of dissolution of high polymers and solvated solutes. Every portion of a lyophilic molecule requires solvation by suitable chemical groups present in the solvent so that the surface of the solute and the solvent may be homologous. Hence the more a lyophilic solute comprises of varied groups, the more is there chance of its exhibiting mix-solvency. The solvation is primarily a dynamic one as pictured by Langmuir, *i.e.*, the solvating group strikes the surface of the big solute molecule, remains hooked there for a small interval of time either by Van der Waals' cohesive forces or by hydrogen bond (Lassetre, *Chem. Rev.*, 1937, 20, 259; Pauling, "The Nature of the Chemical Bond", 1940, p. 284) and then flies off. Before the group, thus left unsolvated, has time to unite with similar others for precipitation, another molecule of solvent strikes and solvates it. Meyer and Mark (*loc. cit.*) point out that dissolution takes place irrespective of the molecular weight of the solute only when the molecules have a stronger attachment for all portions of the high polymer than the portions themselves have for each other. Eirich (*Annual Report for the Progress of Physics*, 1940, 7, 329) also adopts a similar picture for the process of swelling and dissolution of high polymers. In solution practically negligible portion of the molecules may be present as complex molecules or micelles by mutual solvation, but the author believes on various evidences (Palit, *J. Indian Chem. Soc.*, 1940, 17, 537) that the main portion remains, not as micelles, but as highly solvated single molecules.

In this process of specific solvation, roles of the glycol and the alcohols are not well defined. The addition of hydrocarbons like benzene, cyclohexane, etc. has been shown to augment this mix-solvency distinctly. Glycol probably solvates the carboxyl portion and if it is assumed that the sodium ion is attached to the oxygen by electrostatic attraction only, it becomes easy to visualise that glycol solvates this part of the molecule by hydrogen bond as shown below.



The role of alcohol is possibly to solubilise the remaining hydrocarbon chain of the soap molecule, for which it has rather a low solvent power, as shown by the poor solubility of stearic acid in ethyl alcohol (about 2 per 100 parts at 20°). The resulting solvency becomes high only when the hydrocarbon portion of the alcohol covers a considerable portion of the molecule. This explains the increase in molecular weight with increase of mix-solvency. It is not clear, however, why two separate alcohol molecules cannot function in the same way as a single glycol molecule. Perhaps, the two alcohol molecules cannot provide sufficient cover for the ionically bound sodium atom, while one glycol molecule effectively does.

The powerful mix-solvency of A-G-H mixture can be explained as due to the solvation of the hydrocarbon portion of the soap by a powerful solvent, say, benzene. The role of alcohol in A-G-H mixtures then becomes a minor one and consists of simply constituting a common solvent for the immiscible pair, glycol and benzene. It is now apparent why most ordinary organic solvents have very small dissolving power for soap. These solvents can hardly provide simultaneously both types of solvation necessary for the process. Table IV gives an idea of the strikingly small solubilities of soaps in common organic solvents.

The proper test of the theory developed above would be to find out a glycol and a hydrocarbon type solvent which are mutually soluble and to see if they possess power of mix-solvency for soap. A search through literature (Lawrie, "Glycerol and the Glycols", 1928, p. 375) shows that this is possible not with the simplest glycol but with its higher homologues or polyglycols, such as propyleneglycol and diethyleneglycol, which though immiscible with benzene is miscible with powerful hydrocarbon-solvents like chloroform, ethylene dichloride, etc.

An immediate appeal to experiment testified to the correctness of our theory and not only chloroform, but a host of other halogenated hydrocarbons, *e.g.* ethylene dichloride, dichloroethylene, trichloroethylene, tetrachloroethane, etc., exhibited pronounced mix-solvency in combination with these glycols. We shall term such compositions comprising of a polyhydric alcohol and a hydrocarbon or a chlorinated hydrocarbon as G-H mixtures. Thus, mix-solvency for alkali metal soap is shown by A-G, G-H or A-G-H mixture but not to any considerable extent by A-H mixtures.

The solubility data for chloroform-diethyleneglycol or propyleneglycol are given in Table V and represented graphically in Fig. 3. Since acetone has some solvency for hydrocarbons, it is expected according to our views to exhibit mix-solvency for soap in combination with ethyleneglycol. This expectation has been experimentally fulfilled (Fig. 3; Table V). The curves

TABLE IV.

Solubility of soaps in common organic solvents..

| Soap. | Solvent. | Temp. | Solubility. | Observer. |
|---------------------|-------------------|-------|----------------|--------------------------------|
| Potassium stearate | Ethyl alcohol | 10° | 0.432 g./100g. | Chevrenl* |
| Sodium stearate | Do | 10° | 0.200 | |
| Potassium palmitate | 95% Alcohol | 22° | 1.430 | Freundlich* |
| Sodium palmitate | isoPropyl alcohol | 50° | ca. 0.5% | Vold, Legett and McBain° |
| " | Glycerol | 50° | ca. 1.0 | |
| " | Diethyleneglycol | 50° | ca. 1.5 | |
| Lithium palmitate | Ethyl alcohol | 18° | 0.079/100 c.c. | Partheil and Ferie† |
| " | " | 25° | 0.095 | |
| Lithium stearate | " | 18° | 0.041 | |
| " | " | 25° | 0.053 | |
| Lithium palmitate | Methyl alcohol | 25° | 0.771% | Quoted by Jamieson† |
| " | Acetone | 25° | 0.508 | |
| Lithium stearate | Ether | 15.8° | 0.011 | |
| " | Methyl acetate | 25° | 0.439 | |
| " | Acetone | 25° | 0.706 | |
| Ammonium stearate | Ether | 15° | 0.10 | |
| Ammonium palmitate | Ether | 13° | 0.20 | Laing‡ |
| " | Acetone | 13° | 0.20 | |
| " | Alcohol | 10° | 0.70 | |
| Potassium oleate | Alcohol | 18° | 1.24 | |

* Quoted by Lederer, "Kolloidchemie der Seife," 1932, pp. 219-222.

† Jamieson, "Vegetable Fats and Oils", 1932, p. 290.

‡ Laing, *J. Chem. Soc.*, 1918, 113, 435.

strikingly show the effect of mixing a hydrocarbon with a glycol. It is further to be noticed that the maximum solubility for diethyleneglycol—chloroform occurs at about 30% weight of chloroform in the solvent, whereas for propyleneglycol—chloroform it occurs at about 42% weight of chloroform. A calculation from molecular weights shows that these two maxima neither

occur at any simple molecular ratio of the solvents, nor are at equal mol. per cent. for the two combinations (mol. per cent chloroform 27'5 and 31'5 respectively).

FIG. 3.

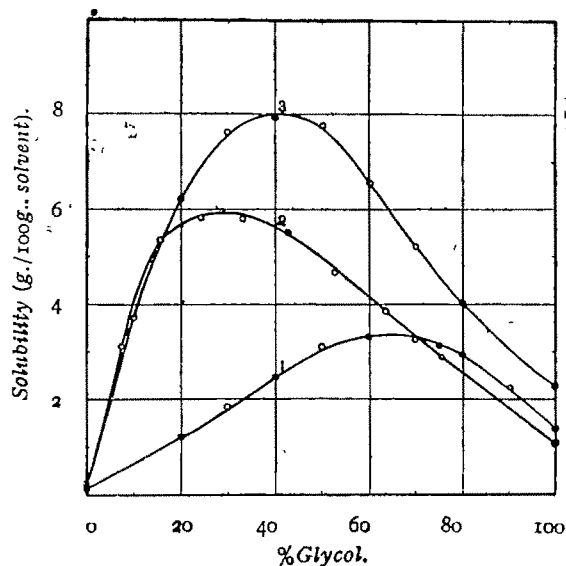


TABLE V.

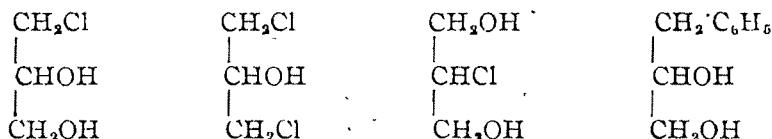
Mix-solubility of sodium stearate in chloroform-glycol mixture at 25°.

| First solvent : glycol (by wt.). | Solubility (g /100 g. solvent). | | |
|-------------------------------------|-----------------------------------|--------------------------------|-----------------------------|
| | Chloroform —diethyleneglycol.* | Chloroform —propyleneglycol | Acetone —ethyleneglycol. |
| 100:0 | 0'22 | 0'22 | 0'14 |
| 90:10 | 3'10 | 3'72 | — |
| 80:20 | 5'31 | 6'21 | 1'21 |
| 70:30 | 5'83 | 7'61 | 1'82 |
| 60:40 | 5'81 | 7'92 | 2'47 |
| 50:50 | 5'50 | 7'75 | 3'10 |
| 40:60 | 4'66 | 6'55 | 3'31 |
| 30:70 | 3'85 | — | 3'27 |
| 25:75 | — | — | 3'13 |
| 20:80 | 2'91 | 4'02 | 2'93 |
| 10:90 | — | — | 2'25 |
| 0:100 | 1'10 | 2'29 | 1'36 |

* With reference to this combination, the first column represents ratios 'by volume' instead of 'by weight'.

An immediate corollary from the above findings is that if the same molecule can combine a glycolic portion as well as a portion having solvent power for hydrocarbons, this compound will be a good solvent for soap, and the more a proper balance between these two characters will be attained in a molecule, the stronger will this compound be in its dissolving power for soaps. As an illustration of this principle, we may compare the structures of ethyleneglycol (I), and propyleneglycol (II) and α -chlorohydrin (VI). The first two compounds have the same type of dihydroxylic structure, except that in (II) one of the hydrogen atoms of the (I) is replaced by a methyl group. As a consequence, propyleneglycol combines the two above-mentioned characteristics much better than ethyleneglycol, and hence, according to our theory, should be more powerful of the two. These deductions from theory are borne out by the fact that the solubility of sodium stearate in ethyleneglycol is 1.36%, whereas in propyleneglycol is 2.3%.

Let us now consider some derivatives of glycerol from this standpoint.



α -Monochlorohydrin. $\alpha\gamma$ -Dichlorohydrin. β -Monochlorohydrin. α -Phenyl $\beta\gamma$ -diol-propane.

(VI)

(VII)

(VIII)

(IX)

The compound (V) is glycerol, which evidently cannot be a very powerful solvent for soap due to its lack of pronounced hydrocarbon-dissolving portion, except of course, the straight hydrocarbon chain $-\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2-$. Hence, it will have some solvency for soap and will be superior to non-hydroxylic solvents, which it is (*vide* Table VI). The second compound, α -monochlorohydrin (VI), obtained by replacement of one hydroxyl group of glycerol by a chlorine atom, may be looked upon as a combination of a glycol and a chlorinated hydrocarbon, which latter types are well known as good solvents for hydrocarbon and paraffin. If one more hydroxyl of glycerol is replaced by chlorine, the resulting molecule, $\alpha\gamma$ -dichlorohydrin (VII) loses this characteristic feature. Hence, we should expect that the solvent power for soap will be in the order of monochlorohydrin > glycerol > dichlorohydrin. This has been experimentally found to be true as the following table shows, where the temperature of formation of isotropic solution with 10% by weight of sodium palmitate has been determined by heating in sealed tubes. The first four data are taken from a paper by Vold, Degett and McBain.

TABLE VI.

| Solvent | Temp. of formation of isotropic soln. with 10% Na-palmitate. | Solvent. | Temp. of formation of isotropic soln. with 10% Na-palmitate. |
|-------------------|--|--------------------------------|--|
| Heptane | 244° | Glycerol | 84° |
| isoPropyl alcohol | 137° | α -Monochlorohydrin | 58° |
| | | | 61° (for Na-stearate). |
| Diethyleneglycol | 91° | $\alpha\gamma$ -Dichlorohydrin | Above 170° (boiling point). |

Some predictions may now be ventured. In comparing the two isomeric monochlorohydrins (see formulae VI and VIII) we find that the main difference between the α - and the β -compound lies in the position of the two hydroxyl groups. Since we have seen in our experiments with trimethyleneglycol that the hydroxyl group must be on the two contiguous carbon atoms to have good latent solvency for soap, we can safely infer that the β -compound will be far less powerful than the α -compound. Suppose we replace a chlorine atom of the α -chlorohydrin by a phenyl group to produce the structure (IX). This compound combines both a glycolic character and a benzenoid character and hence should be a powerful solvent for soap. Attempts are being made to test the validity of these inferences and the results will appear in a later publication.

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A NOTE ON THE CONSTITUTION OF HYPOPHOSPHORIC ACID AND ITS SALTS.

BY JAGANNATH GUPTA AND ANIL KUMAR MAJUMDAR.

This acid, having the empirical formula H_2PO_3 , has been the subject of long controversy with regard to its molecular constitution. From the available data, it is notable that as a general rule the dimeric formula $H_4P_2O_6$ has been derived by workers studying the free acid and its metallic salts and the monomeric H_2PO_3 by those working with organic derivatives.

Investigations on the Raman spectra of this acid and its derivatives have been scanty (Ghosh and Das, *J. Phys. Chem.*, 1932, **36**, 586), doubtless owing to preparative and other experimental difficulties. The results were incomplete and inconclusive. A thorough investigation was undertaken by the present authors but could not be completed in the present abnormal circumstances. Meanwhile, it could be seen that the data already obtained clarified a part of the question definitely, and are therefore being reported here.

Acid sodium hypophosphate was prepared by the method of Cornie as modified by Rosenheim and Pinsker (*Ber.*, 1910, **43**, 2003). This salt crystallised well and was easily obtained pure, but was not very soluble in water. It was converted into the corresponding acid potassium salt through the sparingly soluble acid barium salt by double decomposition with potassium sulphate. An aqueous solution which was nearly of 55% strength was exposed to the mercury arc radiation 4358\AA , using a *m*-dinitrobenzene filter, and the spectrum photographed with a fairly broad slit. A solution of the free acid was obtained through the insoluble lead salt and hydrogen sulphide, and concentrating over sulphuric acid. In this solution, the amount of sulphuric acid present as impurity was negligible, since the strongest breathing frequency of the sulphate ion was not found in the photographed spectrum.

The following Raman lines below 2000 cm^{-1} were recorded with the figures in brackets their approximate relative intensities, compared visually :—

Acid potassium salt : 300 (5), 468 (2), 661 (3), 896 (1), 1084 (4), 1204 (2).

Free acid solution : 300 (3), 475 (1b), 654 (2), 928 (1), 1093 (2), 1175 (1b).

The maximum number of Raman lines permissible for the monomeric formula PO_3'' , on the legitimate assumption that the three oxygen atoms are equivalent with respect to phosphorus, is *four*, corresponding to the

symmetry C_{3v} . It is therefore certain that the acid and its salt in solution contain more complex units. The closely analogous spectra of the acid and the acid salt show that the structures must be very similar. The dimeric *trans* structure seems highly probable for the two following reasons :—

(i) This structure having symmetry D_{3d} gives rise to six Raman frequencies.

(ii) The magnitude and relative intensities of the lines are closely comparable with those for the dithionate ion 275(4), 315(2), 550(1), 706(2), 1090(4), 1215(2b), being shown to possess this type of ionic symmetry by one of the present authors in a previous communication (Gupta and Guha, *Proc. Nat. Inst. Sci. India*, 1941, 7, 267).

It may be pointed out that an alternative explanation of the appearance of the six frequencies on viewing the HPO_3^- ion as a symmetrical top is untenable, on the ground that the acid phosphites do not give rise to more than four frequencies below 2000 cm^{-1} , where the ions are known to contain P-H link and possess unsymmetrical structures (Simon and Feher, *Z. anorg. Chem.*, 1937, **230**, 289).

These results, interesting as they are, are yet insufficient to completely establish the structure of the acid and its derivatives, and a full discussion is deferred pending further work.

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STUDIES ON AERIAL OXIDATION OF COAL WITH SPECIAL REFERENCE TO THE DISTRIBUTION OF OXYGEN AND CARBON IN COAL AND ITS OXIDATION PRODUCTS.

By J. K. CHOWDHURY AND ANIL BHUSAN BISWAS.

Bituminous coking coal samples have been subjected to aerial oxidation at 150° for different periods of time and quantitative distribution of carbon has been investigated in the oxidation products by estimating oxygen in relative groups *e.g.*, OH, CO, COOH.

Coal is an organic colloidal complex which may be resolved into three principal classes of substances, *viz.* (a) bitumen, soluble in organic solvents, (b) humic acids, insoluble in organic solvents but susceptible to oxidation and (c) resistant organic complex, insoluble in organic solvents and resistant to chemical reactions. The bitumens and resistant portions together form only a small fraction of coal. The key to the solution of the difficult problem of constitution of coal is held by the humic acid constituent which constitutes 70-80% of the coal substance.

Very little humic acid can, however, be obtained from mature bituminous coal by treatment with alkali. Evidently the condensation and polymerisation processes involved in the formation of coal have gone very far to form almost insoluble products in these coals. It is, however, found that by careful oxidation, these humic acids may be made soluble in alkali and obtained as regenerated humic acid. As a result of various oxidation and other experiments, it has been suggested by several workers that this regenerated humic acid is constituted mainly of aromatic ring-compounds, condensed together to form a complex nucleus which is associated with outer groupings or side-chains. In the course of oxidation, the outer groupings are first oxygenated giving rise to carboxylic compounds soluble in alkali, which are recovered as regenerated humic acid. The nucleus may be disintegrated by further careful oxidation giving rise to aromatic carboxylic acids, oxalic acid etc., while by too drastic an oxidation, the final products of combustion such as H_2O , CO_2 and CO may be obtained.

In the present investigation, we have studied a sample of bituminous coking coal obtained from Talcher Colliery. Its chemical composition can be expressed by the empirical formula $C_{19}H_{14}O_2$ (calculated on moisture, ash, ammonia, and H_2S free basis). As the amount of humic acid obtained by alkali treatment is very small (2.20%), we have subjected it to careful oxidation by air at 150° for different periods of time and have tried to follow the distribution of carbon quantitatively in the oxidation products and

estimated the oxygen contained in reactive groups such as carboxyl, hydroxyl (both phenolic and alcoholic), carbonyl and methoxyl in the original and in the oxidised coal. As carbon and next to it oxygen are the most important elements in coal, it is desirable to trace how these elements are distributed in coal and its oxidation products. This may also throw some light on the mechanism of oxidation of coal on which considerable difference of opinion exists.

Analysis of coal.

| Proximate analysis (on dry basis). | | Ultimate analysis (on dry ash-free basis). | | |
|---------------------------------------|-----------|---|----------------------|----------|
| | Per cent. | | Per cent. | Ratio. |
| Moisture | ... 10.04 | C | ... 81.34 | |
| Ash | ... 7.49 | H | ... 5.18 | C/H=15.7 |
| Volatile matter.. | 37.14 | N | ... 1.76 | C/O=7.26 |
| Fixed carbon | ... 55.37 | S | ... 0.52 | |
| | | O | ... 11.20 (by diff.) | |

Rational analysis.

(a) Using pyridine as solvent.

| | Per cent. |
|---|-----------|
| α -Fraction (pyridine insoluble) | 81.50 |
| β -Fraction (pyridine soluble but chloroform insoluble) | .. 10.67 |
| γ -Fraction (pyridine and chloroform soluble) | ... 7.83 |

(b) Using benzene as solvent.

| | Per cent. |
|--|-----------|
| Bitumen (benzene soluble) | 10.54 |
| Humic matter (obtained by air oxidation) | ... 77.09 |
| Resistant residues | ... 12.37 |

In the above data, α -fraction indicates the resistant portion of coal together with insoluble humic acids, while the β - and γ -fractions indicate the amount of bitumen including some humic matter. As pyridine is a basic substance and is liable to dissolve some of the humic acid, we have resolved coal into different fractions by using benzene in the place of pyridine and subjecting the benzene-insoluble coal to air oxidation at 150° for 192 hours followed by alkali treatment.

Progressive Oxidation of Coal by Air at 150°

The stepwise oxidation of coal has proved to be one of the most fruitful methods of exploring the composition and ultimate structure of coal. Aerial oxidation of coal has been studied extensively by Wheeler, Kreulen, Fischer and others (Kremlen, *Brennstoff-Chem.*, 1927, 8, 241; Fischer and co-workers, *ibid*, 1932, 13, 1933; Francis and Wheeler, *Safety in Mines Res. Board*, Paper No. 27, 1926). Other slightly stronger oxidising agents

such as nitric acid (Smith and Howard, *J. Amer. Chem. Soc.*, 1935, **57**, 512, 2322), hydrogen peroxide (Francis and Wheeler, *J. Chem. Soc.*, 1925, **127**, 2236), alkaline permanganate (Bone and co-workers, *Proc. Roy. Soc.*, 1930, **A**, **217**, 480), acid permanganate (Francis, *Fuel*, 1938, **17**, 363), chlorine peroxide (*J. Indian Chem. Soc. Ind. News Ed.*, 1940, **3**, 1), pressure oxidation in alkaline solution (Fischer and Schrader, *Ges. Abh. Kennt. Khole*, 1920, **5**, 200, 500) and even electrolytic oxidation (Lynch and Collett, *Fuel*, 1932, **11**, 408) have been used by a large number of workers.

Aerial oxidation of coal under controlled conditions differs from the oxidation by other reagents in that no profound structural changes are likely to result by the former process. The peripheral groups are mainly affected and replaced by COOH groups.

EXPERIMENTAL.

In the present investigation, oxidation of coal was carried out at a temperature of 150°-160° with air, freed from CO₂, blown by means of a Cenco-blower continuously for about 12 days through finely divided coal placed in the middle of a glass combustion tube heated in an electric furnace. After every 12 hours, the tube was taken out, the coal inside was well stirred and the tube replaced. Test samples were taken out periodically and the yield of humic acid was determined by using 4% sodium hydroxide as the solvent. Humic acid was precipitated from the solution by dilute hydrochloric acid, thoroughly washed, and dried in vacuum at 80°

TABLE I.

Air oxidation of coal at 150°.

| Oxidation time. | in Solubility 4% NaOH. | Humic acid re- covered from alkali soln. | subs- Soluble tances | Oxidation time. | in Solubility 4% NaOH. | Humic acid re- covered from alkali soln. | subs- Soluble tances. |
|-----------------|------------------------------|--|----------------------------|-----------------|------------------------------|--|-----------------------------|
| 0 hr. | 2.20% | 0% | 2.20% | 168 hr. | 87.04% | 63.58% | 23.46% |
| 24 | 25.47 | 17.83 | 7.64 | 192 | 87.63 | 62.09 | 25.54 |
| 48 | 42.08 | 31.90 | 10.18 | 216 | 87.03 | 60.50 | 26.53 |
| 72 | 60.95 | 47.62 | 13.33 | 240 | 86.69 | 58.12 | 28.57 |
| 96 | 72.88 | 56.28 | 16.60 | 264 | 85.25 | 57.23 | 28.02 |
| 120 | 81.16 | 60.65 | 21.51 | 288 | 84.72 | 55.54 | 29.18 |
| 144 | 85.36 | 63.61 | 21.75 | | | | |

It appears from Table I that (i) alkali solubility of oxidised coal gradually increases and reaches a maximum after 192 hours and then gradually decreases, (ii) the yield of water-insoluble humic acid reaches a maximum after about 144 hours and then slowly decreases, (iii) yield of water-soluble oxidation products increases continually with the progress of oxidation. Oxalic acid and benzoquinone have been found to be present in water-soluble products and carbon dioxide in the gaseous products of oxidation.

The process of oxidation has also been followed by determination of the weight of oxidised coal and its carbon, hydrogen, oxygen, nitrogen and sulphur contents which are recorded in Table II.

TABLE II.

Change in the weight and composition of coal.

| Oxidation time. | Increase or decrease in wt. | % Composition | | |
|--------------------|--------------------------------|---------------|------|-------------|
| | | C | H. | O, N and S. |
| 0 hr. | 0 | 81.34 | 5.18 | 13.48 |
| 24 | 2.95% | 79.01 | 5.53 | 15.46 |
| 48 | 5.51 | 76.97 | 5.23 | 17.80 |
| 72 | 7.94 | 75.18 | 4.90 | 19.95 |
| 96 | 7.93 | 74.34 | 4.67 | 20.99 |
| 120 | 6.66 | 72.84 | 4.38 | 22.78 |
| 144 | 4.51 | 72.54 | 4.01 | 23.45 |
| 168 | 2.01 | 71.99 | 3.85 | 24.16 |
| 192 | -0.52 | 71.56 | 3.65 | 24.76 |
| 216 | -2.03 | 70.70 | 3.46 | 25.84 |
| 240 | -3.34 | 70.01 | 3.36 | 26.63 |
| 264 | -4.21 | 69.63 | 3.23 | 27.14 |
| 288 | -5.18 | 69.15 | 3.13 | 27.72 |

From the above table it will be observed that the oxidation of coal may be divided into three distinct periods. In the first, there is an increase in the weight of coal, in the second, there is an equilibrium in the increase in weight due to fixation of oxygen and loss due to escape of gaseous products of oxidation, and in the third there is a gradual increase in the loss of weight. Thus on the one hand, there is formation of humic acid in gradually increasing amounts due to absorption of oxygen and on the other hand there is decomposition of humic acid so formed. Up to 144 hours, the rate of formation of humic acids predominates over the rate of decomposition. After that period, the decomposition of humic acids predominates. The

percentage of carbon and hydrogen steadily decreases with the progress of oxidation, while that of oxygen (including nitrogen and sulphur) gradually increases, the increase being more than double in course of 12 days. The higher hydrogen content observed after 24 and 42 hours of oxidation is perhaps due to incomplete removal of moisture from the hygroscopic products. Considering the increase or decrease in weight of oxidised coal and its composition, it is possible to find out the amounts of carbon, hydrogen, and oxygen present in the oxidised coal and to compare these amounts with the percentages present in the original coal. Any decrease in carbon and hydrogen contents is due to the loss of CO_2 and H_2O , while the increase in oxygen content is due to addition of oxygen to the coal substance. These will be clear from the following data calculated from Table II.

TABLE III.

Amounts of C, H and O present in oxidised coal.

| Oxidation time. | Amounts of different elements present in oxidised coal on the basis of 100 g original coal. | | | Loss or gain of different elements. | | |
|-----------------|---|---------|-------------|-------------------------------------|--------|-------------|
| | C | H. | O, N and S. | C. | H. | O, N and S. |
| 0 hr | 81.34 g. | 5.18 g. | 13.48 g. | 0% | 0% | 0% |
| 24 | 81.30 | — | 15.92 | — 0.05 | — | +18.10 |
| 48 | 81.21 | — | 18.78 | — 0.16 | — | +39.32 |
| 72 | 81.08 | — | 21.54 | — 0.32 | — | +59.89 |
| 96 | 80.23 | 5.04 | 22.19 | — 1.36 | — | +64.68 |
| 120 | 77.67 | 4.67 | 24.30 | — 4.51 | — 9.82 | +81.27 |
| 144 | 75.78 | 4.19 | 24.50 | — 6.83 | —19.09 | +81.79 |
| 168 | 73.41 | 3.93 | 24.64 | — 9.76 | —24.11 | +82.79 |
| 192 | 71.19 | 3.66 | 24.63 | —12.47 | —29.31 | +82.78 |
| 216 | 69.26 | 3.39 | 25.31 | —14.85 | —34.56 | +87.91 |
| 240 | 67.83 | 3.17 | 25.74 | —16.62 | —38.80 | +90.95 |
| 264 | 66.70 | 3.09 | 25.99 | —18.00 | —40.35 | +92.80 |
| 288 | 65.58 | 2.97 | 26.28 | —19.36 | —42.66 | +94.85 |

Table III indicates that the rate of removal of hydrogen is greater than that of carbon. The loss of carbon and hydrogen is due to the escape of CO_2 and H_2O . The amount of CO_2 escaping up to 4 days is very small (1.36% only) though the amount of oxygen found in the oxidised coal rapidly increases to about 65%. A critical state of oxidation is apparently reached at this stage and further additions of oxygen are accompanied by

increase in the loss of carbon as CO_2 and hydrogen as H_2O . About 20% of carbon and over 40% of hydrogen of the coal are removed in course of 12 days.

Distribution of Oxygen in Coal and in Humic Acid obtained from Oxidised Coal.

It will be observed that in the course of oxidation, the oxygen content of coal increased from 11.2% to about 25.5%. In order to see how this oxygen is distributed in the form of oxygen-containing groups such as carboxyl, hydroxyl, methoxyl and carbonyl, these radicals were quantitatively determined in coal and in humic acid obtained from oxidised coal. Analysis of samples of humic acid extracted from different stages of oxidised coal indicated a fair degree of constancy of composition (Table IV). This constancy is achieved after 144 hours of oxidation with an oxygen content of about 36%. A critical state is reached at this stage, and further oxidation breaking down the humic acid into carbon dioxide and water. It is interesting to note that no nitrogen or sulphur is lost by this oxidation as practically the whole of sulphur in the original coal is found in the humic acid.

TABLE IV.

Composition of the recovered humic acids.

| Hours of oxidation of coal. | Yield of humic acid. | Composition of humic acid | | |
|--------------------------------|-------------------------|---------------------------|-------|---------------------------|
| | | C | H. | O (including N and S). |
| 48 | 31.90% | 62.02% | 3.06% | 34.92% |
| 144 | 63.61 | 60.98 | 2.98 | 36.01 |
| 192 | 63.58 | 61.01 | 3.00 | 35.99 |
| 288 | 55.54 | 60.03 | 2.97 | 37.00 |

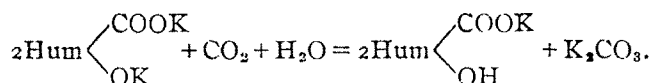
Determination of Carboxyl and Hydroxyl Groups.—The usual method for the determination of carboxyl and total hydroxyl is to methylate the product exhaustively and then to find out the total methoxyl by Zeisel's method and the ester methoxyl by saponification. The ether methoxyl is then found out by difference. But methylation by means of methyl alcohol and hydrochloric acid has been found to be incomplete. Diazomethane, though somewhat better, has also been found to cause incomplete methylation by several workers, due probably to steric hindrance found in several aromatic acids. We have, therefore, followed the following three methods which have been found by Ubaedini (*Brennstoff. Chem.*, 1930, 18, 273) to give satisfactory results.

(I) Total COOH and phenolic OH were found out by titration with alkali under the following conditions.

Humic acid was treated with excess of alcoholic $N/5$ KOH (using 95% alcohol), when potassium humate, formed by neutralisation of COOH and phenolic OH groups, precipitated. It was filtered off and the excess of alkali in the filtrate was titrated using phenolphthalein as indicator. This gives the amount of alkali required to neutralise the total carboxylic and phenolic OH groups.

Phenolic OH group was then determined separately as follows :—

The above precipitate of potassium humate was suspended in alcohol and a stream of carbon dioxide was passed through it when free phenolic groups were liberated according to the following reaction,

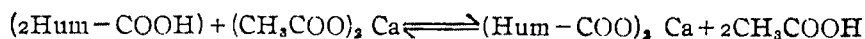


The strength of alcohol was carefully regulated so as not to fall below 75%. Under these conditions potassium humate containing free phenolic groups remained insoluble while K_2CO_3 went into solution. This was filtered and washed with 75% alcohol. Estimation of potassium carbonate in the filtrate gave figures for phenolic OH (method *a*), while estimation of potassium in the precipitate gave figure for carboxyl groups (method *b*).

(a) The amount of potassium carbonate in the filtrate was determined by adding excess of acid and titrating back the excess with $N/10$ -KOH. (Direct titration of the carbonate solution was not possible owing to light yellow colour of the filtrate). The value of phenolic OH was obtained directly from amount of potassium carbonate found and that of carboxyl was found by difference.

(b) Carboxyl group was also determined directly by collecting the precipitate of potassium humate containing free phenolic group in a platinum crucible and gently igniting the same to ash. The alkali (K_2O) in the ash was estimated by titration. This alkali gave the amount of carboxyl groups present in humic acids. Phenolic OH was found by difference.

(II) In the second process, carboxyl groups were estimated directly by treating humic acid with a solution of calcium acetate when calcium humate was formed and free acetic acid liberated.



In order to complete this reaction, it was necessary to remove the free

acetic acid as soon as it was formed. This was done by adding finely powdered calcium carbonate according to the following reaction,



The carbon dioxide evolved in the above reaction was swept forward by air, free from carbon dioxide and estimated by absorption in caustic potash bulbs. It will be seen that one molecule of carbon dioxide is equivalent to two carboxyl groups in the humic acid.

(III) The total OH groups (both phenolic and alcoholic) present in the substance were estimated by acetylating with acetic anhydride and pyridine. By deducting the phenolic OH, found by the previous methods, the value of alcoholic OH was obtained. The data are given in the following table.

TABLE V.

| Method of estimation. | Humic acid | | | Coal | | |
|-----------------------|------------------|----------|-------|------------------|----------|--------|
| | Hydroxyl groups. | | | Hydroxyl groups. | | |
| | Total. | Phenolic | Alc. | Total | Phenolic | Alc |
| I(a) | ... | 6'32% | ... | 24'06% | .. | 0'093% |
| I(b) | ... | 6'11 | ... | 25'39 | .. | 0'12 |
| II | ... | ... | ... | 23'08 | ... | ... |
| III | 6'41% | 6'21 | 0'20% | ... | 2'08% | 0'11 |

The above data show that fairly concordant values are obtained for humic acids but not for coal. Too small values are obtained in the case of coal particularly by method II, due presumably to incomplete reaction between the insoluble coal substance and calcium acetate. Hence only a small fraction of total oxygen in coal can be accounted for (Table VII).

Estimation of Carbonyl Groups.—Carbonyl groups have been estimated by treatment with phenylhydrazine, the excess of which is determined by means of Fehling's solution. The precipitated cuprous oxide was collected and estimated by titration with potassium permanganate (Strache and Harrancourt, *Brennstoff-Chem.*, 1924, 5, 350). The amounts of carbonyl groups found in humic acid and coal are 3'54% and 0'12% respectively. No methoxyl groups have been detected either in coal or in humic acid.

Oxygen Balance of Humic Acid and Coal.

From the above data it is possible to calculate the amount of oxygen found in various reactive groups in the coal substance and in the humic acids examined. The following table collated from the previous data gives an idea of the oxygen in the various groups.

TABLE VI.

| Reactive groups | Humic acid | | Coal | |
|------------------|------------|---------------------------|---------|---------------------------|
| | Amount. | Fraction of total oxygen. | Amount. | Fraction of total oxygen. |
| Total oxygen | 32.87% | — | 11.2% | — |
| Oxygen in COOH | 16.98 | 51.6% | 0.633 | 5.65% |
| „ „ phenolic OH | 6.03 | 18.3 | 0.1 | 0.888 |
| „ „ alcoholic OH | — | — | 1.85 | 16.52 |
| „ „ CO group | 2.02 | 6.14 | 0.07 | 0.62 |
| Oxygen accounted | 25.04 | 76.04 | 2.67 | 23.77 |
| „ unaccounted | 7.83 | 23.96 | 8.53 | 76.23 |

It will be found that 76.04% of the total oxygen in humic acid have been accounted for, while the amount of oxygen accounted for in coal amounts to 23.77% only. The unaccounted oxygen is apparently due to stable ether or cyclic oxygen. The presence of such stable oxygen linkage has also been suggested by other investigators (Kasehagen, *Ind. Eng. Chem.*, 1937, **29**, 600; Fischer and Eisner, *ibid.*, 1937).

From the above data it is possible to get an idea regarding the process of aerial oxidation of coal. The major portion of oxygen in oxidised coal is found in -COOH- groups. It will be seen from previous data that the COOH groups in coal increased from 4.7% to 24.8%, phenolic OH from 0.11% to 6.28% and the ketonic (CO) groups from 0.12% to 3.54% in the course of oxidation. Apparently the external groupings in coal are oxidised giving place to carboxyl groups and the phenolic (OH) and ketonic (CO) groups are also considerably increased. Surprisingly, however, no increase in the alcoholic OH groups has been found during oxidation. On the contrary a slight decrease from 1.97% to 0.2% was observed. It is likely that alcoholic groups are immediately further oxidised giving rise to carboxyl groups.

Equivalent Weight of Humic Acid.—100 G. of humic acid contain 3.54 g. i.e., 0.126 mol. of CO (Table VI). Hence for at least one CO group in humic acid per molecule, the equivalent weight becomes 800.

As 100 g. of humic acid contain 24.8 g. or 0.55 mol. of COOH and 6.21 g. of phenolic OH i.e., 0.375 mol., the ratio of carbonyl, hydroxyl and carboxyl groups in the humic acid molecule becomes 2:6:9 and its molecular weight becomes 1600.

Distribution of Carbon in the Oxidation Products of Coal.

Determination of the yield and carbon content of various products obtained after 144 and 192 hours of oxidation enabled us to determine quantitatively how carbon is affected in the course of oxidation. The gaseous product

(i.e. CO_2) was determined by absorption in potash bulbs, while the oxidised coal was resolved into different fractions by treatment with 4% alkali and acidification of the filtrate. Carbon content of solid products was determined by combustion, while that of the solution by oxidation with potassium dichromate. The distribution of carbon in various fractions is given below.

TABLE VII.

| | | Carbon content after oxidation for | |
|--|-----|------------------------------------|------------|
| | | 144 hours: | 192 hours. |
| Carbon as CO_2 | .. | 6.37% | 9.37% |
| as water-soluble organic compounds | .. | 24.39 | 33.52 |
| as humic acids | ... | 54.8 | 45.56 |
| resistant residues (i.e. not dissolved in 4% alkali) | | 12.50 | 10.37 |
| unaccounted | .. | 1.40 | 2.02 |

Mechanism of Aerial Oxidation.—It will be observed that in the course of oxidation, the oxygen content of the oxidised coal slowly increased by more than 100% and carbon dioxide was evolved at the same time. The increase in oxygen content is mostly due to the formation of humic and water-soluble acids. If the view that the coal consists of a nuclear complex of condensed aromatic rings with side-chains be accepted, it may be visualised that oxygen first enters the side-chain forming alcoholic groups which are unstable and quickly disappear giving place to carboxyl groups. As a result practically no alcoholic group can be detected in humic acid. The chemical composition of humic acid consisting of carboxyl and phenolic hydroxyl groups and perhaps one ketonic group remains practically constant. The yield of humic acid increases with the progress of oxidation but after 144 hours slowly decreases while the yield of water-soluble acids increases continuously. Evidently in humic acid, the side-chains have been replaced by carboxyl and new phenolic groups have been formed by oxidation. With the progress of further oxidation, the nucleus is attacked at the phenolic groups and is opened up forming carbon dioxide and water-soluble acids.

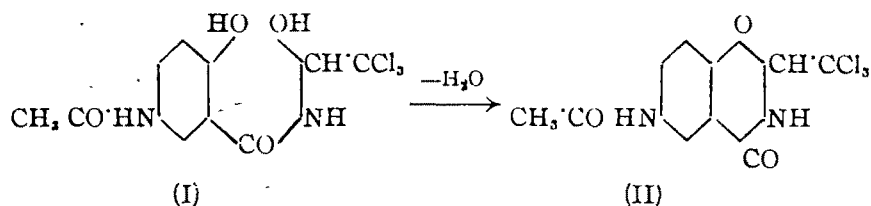
ON CHLORALAMIDES. CHLORAL-5-ACETAMIDO-SALICYLAMIDE AND RELATED COMPOUNDS.

BY K. N. RANA.

5-Acetamidosalicylamide has been condensed with chloral to yield the usual product of the type $R \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3$. The acetamido group, unlike the negative groups, in the position 5 does not inhibit the condensation.

Chloral-5-acetamidosalicylamide gives with dimethyl sulphate, benzoyl chloride and acetic anhydride, the related derivatives, and, on dehydration, 6-acetamidobenzo-2-trichloromethylmetoxazone.

5-Aminosalicylamide does not condense with chloral to give a simple aldol type condensation product, $R \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3$, due to the complication brought about by the highly active amino group (cf. Wallach, *Ber.*, 1871, **4**, 668; Hirwe and Kulkarni, *Proc. Indian Acad. Sci.*, 1941, **18A** 49). However, 5-acetamidosalicylamide easily condenses on heating with a moderate excess of chloral to yield quantitatively chloral-5-acetamidosalicylamide (I).



The condensation product (I) retains the phenolic group and decomposes at its melting point into the amide and chloral. But as the substituent $-NH \cdot CO \cdot CH_3$ in the position 5 is not much of a negative nature, the chloral-amide unlike chloral-5-chlorosalicylamide (Hirwe and Rana, *Ber.*, 1939, **72**, 1346) is sufficiently stable in every respect.

Thus, it is observed that the formation, as also the stability, of the variously 5-substituted chloralsalicylamides depends on the nature of the substituents; the negative substituents in the position 5 inhibit the condensation (Hirwe and Rana, *loc. cit.*; Hirwe, Gavankar and Patil, *Proc. Indian Acad. Sci.*, 1940, **11A**, 512), but it is promoted as the substituents tend to become positive.

Hirwe and Wagh (*private communication*) attempted to condense 3-acetamidosalicylamide with chloral, but obtained no definite product. This result is interesting and indicates that although the negative substituents

in the position 3 promote the condensation, the tendency deteriorates as the substituents become positive.

On dehydration with cold, concentrated sulphuric acid, chloral-5-acetamidosalicylamide (I) gives 6-acetamidobenzo-2-trichloromethylmetoxazone (II); insolubility in alkalis and absence of colouration with ferric chloride support the ring formation. The latter does not hydrolyse with ammonia to yield the corresponding α -amino compound, like 6:8-dichlorobenzo-2-trichloromethylmetoxazone (Hirwe and Rana, *J. Univ. Bombay*, 1939, 8, iii, 243); hot alcoholic ammonia decomposes it in an unrestrained fashion. It gives a monoacetyl derivative, but no hydrochloride.

The compound (I) gives with dimethyl sulphate and benzoyl chloride the corresponding derivatives; but, when heated with acetic anhydride and two drops of concentrated sulphuric acid, it yields 6-acetamidobenzo-2-trichloromethylmetoxazone (II) and its acetyl derivative, instead of the usual diacetyl derivative which, however, is obtained when the chloralamide is treated with acetic anhydride at 0° in 10% sodium hydroxide solution, this procedure generally helping the formation of either an α -anhydro derivative, or a benzometoxazone (Hirwe and Rana, *J. Univ. Bombay*, 1938, 7, iii, 174; 1939, 8, iii, 243).

EXPERIMENTAL.

Condensation of 5-Acetamidosalicylamide with Chloral: Chloral-5-acetamidosalicylamide.—A mixture of powdered 5-acetamidosalicylamide (5 g.) and chloral (15 c.c.) in a boiling tube, fitted with an air condenser, was gently heated on a wire gauze, until the clear solution suddenly solidified. It was kept at the room temperature overnight and then poured into ice-water, triturated, filtered off, washed and dried. The compound, soluble readily in methanol, alcohol, glacial acetic acid and acetone, sparingly in chloroform, benzene, and difficultly in hot water and ether, crystallised from alcohol in colourless, shining prisms, m.p. $176-77^\circ$ (decomp.), yield 6 g. It gave a violet colouration with ferric chloride. (Found: C, 39.00; H, 3.27; N, 8.23; Cl, 31.01. $C_{11}H_{11}O_4N_2Cl$, requires C, 38.66; H, 3.25; N, 8.21; Cl, 31.16 per cent).

Dehydration of Chloral-5-acetamidosalicylamide with Concentrated Sulphuric Acid: 6-Acetamidobenzo-2-trichloromethylmetoxazone.—Powdered chloral-5-acetamidosalicylamide (5 g.) was dissolved in concentrated sulphuric acid (20 c.c.) in the cold, and the solution kept inside a desiccator for 24 hours. When it was poured on to crushed ice, a white solid separated which was filtered off, washed and dried. The solid, soluble in methanol, alcohol, acetone, glacial acetic acid and benzene, crystallised

from alcohol in white, shining plates, m.p. $218-19^{\circ}$, yield 4 g. It gave no colouration with ferric chloride. (Found: C, 41.18; H, 2.96; N, 8.95; Cl, 32.94. $C_{11}H_9O_3N_2Cl_3$ requires C, 40.81; H, 2.81; N, 8.66, Cl, 32.90 per cent).

The *acetyl derivative*, prepared from the above compound (1 g.), acetic anhydride (5 c.c.) and concentrated sulphuric acid (2 drops), crystallised from alcohol in white, fine needles, m.p. $197-98^{\circ}$. It gave no colouration with ferric chloride. (Found: Cl, 29.10. $C_{13}H_{11}O_4N_2Cl_3$ requires Cl, 29.12 per cent).

α -Methoxychloral-5-acetamido-2-methoxybenzamide.—To a solution of chloral-5-acetamidosalicylamide (2 g.) in sodium hydroxide (20 c.c., 10% solution) at 0° was added dimethyl sulphate (2 g.) with constant shaking. The mixture was kept overnight in a refrigerator, when a paste separated, which solidified on long standing with water. The solid, soluble in methanol, alcohol, acetone and glacial acetic acid, crystallised from alcohol in colourless needles, m.p. $166-67^{\circ}$. It gave no colouration with ferric chloride. (Found: Cl, 29.01. $C_{13}H_{13}O_4N_2Cl_3$ requires Cl, 28.82 per cent).

α -Benzoyloxychloral-5-acetamido-2-benzoyloxybenzamide.—Chloral-5-acetamidosalicylamide (2 g.), when treated as above with benzoyl chloride (2 g.), gave a paste which solidified on triturating with dilute sodium carbonate solution and on standing with water in a refrigerator for a long time. The solid, soluble in methanol, alcohol, acetone and benzene, separated from methanol as a white powder, m.p. $187-88^{\circ}$. It gave no colouration with ferric chloride. (Found: Cl, 19.66. $C_{26}H_{19}O_6N_2Cl_3$ requires Cl, 19.36 per cent).

α -Acetoxychloral-5-acetamido-2-acetoxymethylbenzamide.—Chloral-5-acetamidosalicylamide (2 g.), under a similar treatment as above, with acetic anhydride (2 g.) gave a solid which is soluble readily in alcohol, acetone, glacial acetic acid and sparingly in benzene. It crystallised from alcohol in colourless needles, m.p. $212-14^{\circ}$, and gave no colouration with ferric chloride. (Found: Cl, 24.93. $C_{15}H_{15}O_6N_2Cl_3$ requires Cl, 25.00 per cent).

6-Acetamidobenzotrichloromethylmetoxazone.—A mixture of chloral-5-acetamidosalicylamide (2 g.), acetic anhydride (5 c.c.) and concentrated sulphuric acid (2 drops) was heated in a boiling tube fitted with an air condenser on a water-bath for 2 hours. The dark brown liquid that resulted was poured into boiling water, when a solid was obtained, soluble in methanol, alcohol, acetone, glacial acetic acid and benzene. It gave no colouration with ferric chloride and was found to be a mixture of the above benzometoxazone and its acetyl derivative. They were separated

by fractional crystallisation from alcohol in which the latter is less soluble and identified by taking mixed melting points with authentic specimens of the substances prepared above.

Methyl 5-acetamidosalicylate was prepared from methyl 5-amino-salicylate by the action of acetyl chloride in pyridine medium (Einhorn and Hollandt, *Annalen*, 1898 **301**, 111). It separated as needles from alcohol, m.p. 147-48°.

5-Acetamidosalicylamide.—Methyl 5-acetamidosalicylate (20 g.) and liquor ammonia (200 c.c., d 0.888) were mixed together in a pressure bottle and mechanically shaken for 6 hours, when a dark solution was obtained. It was concentrated on a water-bath to obtain a solid which was triturated with dilute hydrochloric acid, filtered off, washed and dried. The solid, soluble in hot water, alcohol, acetone and glacial acetic acid, crystallised from hot water in colourless needles and from alcohol in square plates, m.p. 204.6°, yield 16.5 g. It was found to crystallise with one molecule of water which it lost at 110° falling into powder. It gave a violet colouration with ferric chloride. (Found: C, 50.82; H, 5.64; N, 13.40; H_2O , 8.58. $C_9H_{10}O_3N_2 \cdot H_2O$ requires C, 50.94; H, 5.66; N, 13.21; H_2O , 8.49 per cent).

The late Prof. N. W. Hirwe was keenly interested in these investigations, and from him the author had received much valuable advice.

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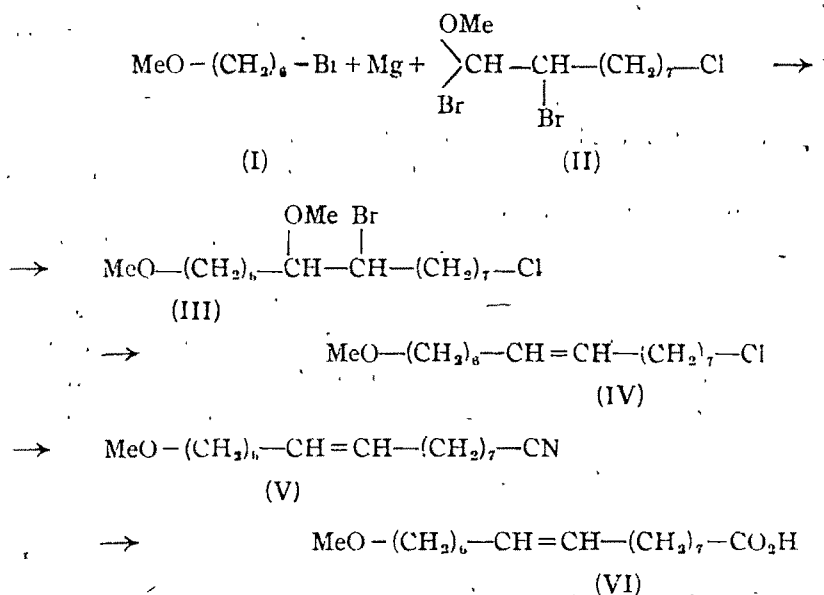
STUDIES IN LONG-CHAIN ACIDS. PART V. ON ALEURITIC ACID.

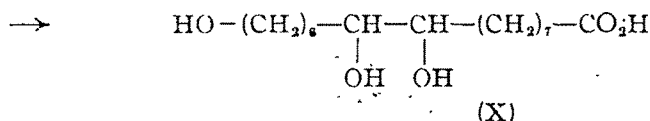
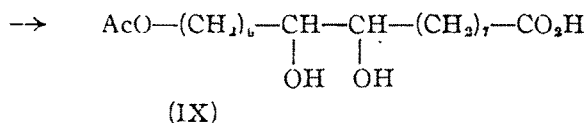
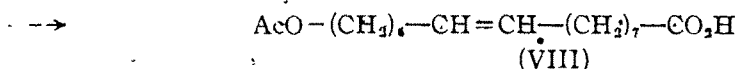
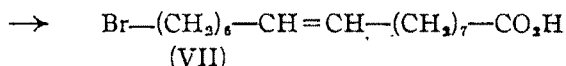
BY P. C. MITTER AND SAILENDRAMOHAN MUKHERJEE

ω -Methoxy 9:10-hexadecenoic acid, intermediate product in the synthesis of aleuritic acid, has been synthesised, starting from ω -methoxyhexyl bromide and 9-methoxy-8 : 9-dibromononyl chloride.

Aleuritic acid is one of the most important constituents of shellac resin obtained by its hydrolysis. Nagel assigned the structure (X) to aleuritic acid based on analytical experiments (*Ber.*, 1927, **60**, 605), but the synthesis of this acid has not yet been achieved. Mitter and Dutt (*J. Indian Chem. Soc.*, 1939, **16**, 673) attempted to synthesise the acid over ω -phenoxy-10-keto hexadecoic acid, but without success.

Noller and Bannerot (*J. Amer. Chem. Soc.*, 1934, **56**, 1563) have synthesised oleic acid by taking advantage of the Boord's reaction (Shoemaker and Boord, *ibid.*, 1931, **53**, 1505) for the introduction of a double bond in a carbon chain. We have successfully synthesised ω -methoxy-9 : 10-hexadecenoic acid (VI) following the reactions similar to those adopted by Noller and Bannerot (*loc. cit.*) for the synthesis of oleic acid. Our scheme for the synthesis of aleuritic acid is as follows :—





ω -Methoxyhexyl bromide (I) has been prepared from the corresponding alcohol which in its turn is obtained by the Bouveault reduction of ethyl ω -methoxyhexoate. An attempt has been made to prepare ω -methoxyhexyl alcohol by the action of the Grignard reagent from methoxy propyl bromide on trimethylene chlorohydrin, according to the method of Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 232), but unfortunately the desired product could not be obtained satisfactorily. Ethyl ω -hydroxyhexoate is prepared by the oxidation of cyclohexanone (Robinson, *J. Chem. Soc.*, 1937, 371) with Caro's acid. The hydroxy-ester on treatment with phosphorus tribromide and pyridine (*cf.* Robinson, *J. Chem. Soc.*, 1937, 723) gives the bromo-ester which with sodium methoxide under specified condition (see experimental) yields the desired ethyl ω -methoxy hexoate in good yield. The reduction of ethyl ω -methoxyhexoate with sodium and ethyl alcohol presents no difficulty provided that the alcohol used is dried over calcium (*cf.* Rydon, *J. Chem. Soc.*, 1936, 594) ω -Methoxyhexyl alcohol, thus obtained, is converted into the corresponding bromo compound (I) by means of phosphorus tribromide and pyridine. For the preparation of 9-methoxy-8, 9-dibromononyl chloride (II), we first tried to oxidise aleurityl alcohol by lead tetra-acetate (Criegee, *Ber.*, 1931, **64**, 260). On being reduced with sodium and sodium-dried butyl alcohol, ethyl aleuritate gives a solid tetra-ol in moderate yield but the oxidation with lead tetra-acetate proves to be most unsatisfactory and the yield of the desired product namely ω -hydroxynonyl aldehyde is so poor that the process has been abandoned in favour of the method of Noller and Bannerot (*loc. cit.*) namely the ozonisation of 9 : 10-octadecenyl chloride.

The compound (III), obtained by the reaction between the Grignard reagent from ω -methoxyhexyl bromide and 9-methoxy-8 : 9-dibromononyl

chloride, is not isolated but the crude product is subjected to zinc dust treatment in butyl alcohol (*cf.* Noller and Bannerot, *loc. cit.*). The product (IV), namely ω -methoxy-8:9-pentadecenyl chloride, is purified by repeated fractional distillation in *vacuo* and is converted into the corresponding nitrile by treatment with sodium cyanide in alcoholic solution. The crude nitrile is hydrolysed with 20% alcoholic potassium hydroxide. The overall yield of this acid is so very poor that further progress could not be made. Experiments are in hand to prepare large amount of this acid in order to complete the synthesis of aleuritic acid.

EXPERIMENTAL.

Ethyl ω -hydroxyhexoate was prepared by the method of Robinson (*J. Chem. Soc.*, 1937, 371).

Ethyl ω -Bromohexoate.—Phosphorus tribromide (10 c.c.) was added dropwise in the cold to a flask containing ethyl ω -hydroxyhexoate (27 g.), dry benzene (10 c.c.) and a few drops of pyridine. The reaction mixture was allowed to stand overnight and then refluxed on the water-bath for $\frac{1}{2}$ hour. After cooling, the mixture was diluted with water, extracted with benzene and the benzene layer washed with sodium bicarbonate solution and water, dried over calcium chloride and the solvent removed. The residue was distilled at 128-30°/16 mm., yield 23 g. (Found: Br, 35.4. $C_8H_{16}O_2Br$ requires Br, 35.87 per cent).

Ethyl ω -Methoxyhexoate.—To a solution of sodium methoxide (from 3.7 g. sodium and 85 c.c. dry methyl alcohol), chilled in a freezing mixture (-15°), were added ethyl ω -bromohexoate (35 g.) drop by drop. The mixture was allowed to stand overnight and then refluxed for 12 hours when the solution assumed a red colour. The mixture was diluted with water, extracted with ether, the ethereal layer washed and dried ($CaCl_2$) and the solvent removed. The residue on vacuum distillation gave 18 g. of ethyl ω -methoxyhexoate, b.p. 94-95°/15 mm. (Found: C, 61.82; H, 10.46. $C_8H_{16}O_2$ requires C, 62.07; H, 10.34 per cent).

ω -Methoxyhexyl Alcohol.—To a warm solution of ethyl ω -methoxyhexoate (23 g.) in calcium-dried alcohol (275 c.c.) sodium (22 g.) was added all at once. After the initial vigour of the reaction had subsided the mixture was heated on an oil-bath until the whole of sodium went into solution (4 to 5 hours). The contents of the flask were then allowed to attain room temperature, 18 c.c. of water added and the heating under reflux continued for 1 hour. Then further water (130 c.c.) was added and the solution heated for another hour. The solution was then steam-distilled. The residue left after the removal of alcohol was diluted with

water, saturated with sodium chloride and extracted three times with ether, the ethereal extract washed, dried (sodium sulphate), the solvent evaporated and the residue distilled in *vacuo*, when a colourless mobile liquid came over at $112^{\circ}/18$ mm., yield 11 g. (Found : C, 63.2 ; H, 11.9. $C_7H_{16}O_2$ requires C, 63.63 ; H, 12.1 per cent).

ω-Methoxyhexyl Bromide (I).—The above alcohol (6 g.) and pyridine (1.5 c.c.) were added in course of 15 minutes to phosphorus tribromide (4.5 g.) and 1 c.c. pyridine and the mixture well-stirred and maintained at 0° . Stirring was continued for 1 hour and the mixture kept overnight. After the addition of ice-water the product was extracted with ether. The extract was washed with acid and then with aqueous sodium carbonate and water, dried over sodium sulphate, the solvent removed and it was distilled in vacuum, b.p. $98-99^{\circ}/19$ mm., yield 5.5 g. (Found : Br, 41.42. $C_7H_{18}OBr$ requires Br, 41.02 per cent).

Aleurityl Alcohol.—Sodium (12.5 g.) was added all at once to a warm solution of ethyl aleuritate (25 g.) in butyl alcohol (210 c.c.). After the initial vigour subsided, the flask was heated on an oil-bath (180°) until the whole of sodium went into solution (3-4 hours). After cooling water (9 c.c.) was added and refluxing continued for 1 hour. Water (62 c.c.) was then added and the mixture heated for another hour. The contents of the flask were then subjected to steam-distillation until the whole of butyl alcohol was driven off. The residual liquid was then extracted three times with ethyl acetate, the extract dried over sodium sulphate and the solvent removed. The residue on cooling solidified. It was crystallised from petroleum ether ($40^{\circ}-60^{\circ}$), m.p. 56° . (Found : C, 66.22 ; H, 11.57. $C_{18}H_{34}O_4$ requires C, 66.2 ; H, 11.7 per cent).

Oxidation of Aleurityl Alcohol with Lead Tetraacetate.—The above alcohol (10 g.) was dissolved in acetic acid (100 c.c.) distilled over chromic acid and the solution was treated at $15-20^{\circ}$ with lead tetra-acetate (33 g.), which was added in portions after which the reaction mixture was heated for 2 hours more at $40-45^{\circ}$. After the lead tetra-acetate was filtered, the filtrate was diluted with water and shaken with ether, the ether solution thoroughly washed and dried over sodium sulphate. The residue after the evaporation of ether was distilled in *vacuo* when only a few drops of *ω*-hydroxy nonyl aldehyde were obtained, b.p. $102^{\circ}/4$ mm.

ω-Methoxy-8 : 9-pentadecenyl Chloride (IV) —8 : 9-Dibromo-9-methoxynonyl chloride (8 g. prepared according to the method of Noller and Bannerot), was diluted with dry ether (20 c.c.). This solution was added drop by drop to the cooled Grignard solution prepared from *ω*-methoxyhexyl bromide (12 g.) and magnesium (1.5 g.) in 25 c.c. of

dry ether. The mixture was allowed to warm up to room temperature, allowed to stand overnight and then decomposed with ice and ammonium chloride and the product after washing and evaporation of the ether was heated for 1 hour at $60^{\circ}/5$ mm. It was pale yellow in colour.

The above product without further purification was dissolved in dry butyl alcohol (40 c.c.) and refluxed for 10 hours with zinc dust (10 g.). After removal of zinc the solution was washed with hydrochloric acid and water and distilled. After three fractionations 2 g. were obtained, b.p. $198-204^{\circ}/5$ mm. (Found: Cl, 12.23. $C_{18}H_{31}OCl$ requires Cl, 12.93 per cent).

ω -Methoxy-9:10-hexadecenitrile.—To the solution of the chloro compound (2 g.) in 17 c.c. of 95% alcohol was added sodium cyanide (1 g.) and a pinch of sodium iodide. The mixture was refluxed for 90 hours, poured into water, extracted with ether and the extract washed and dried. The residue left after the removal of the solvent was subjected to the next treatment without further purification.

ω -Methoxy-9:10-hexadecenoic Acid (VI).—The above nitrile was refluxed for 90 hours with alcoholic potassium hydroxide (50 c.c., 20%). The solution was diluted and extracted with ether to remove any unreacted nitrile. The aqueous layer was acidified and extracted with ether, the extract washed and dried over sodium sulphate. After the evaporation of the solvent, the residue was distilled in vacuum when it came over at $194^{\circ}/2$ mm. (Found: C, 71.62; H, 10.8. $C_{17}H_{32}O_2$ requires C, 71.83; H, 11.27 per cent).

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THE USE OF TRICHLOROACETIC ACID FOR THE EXTRACTION OF PHYTIN OF FOODSTUFFS.

BY M. L. SARMA.

A method for the estimation of the phytin content of foodstuffs is described, in which trichloroacetic acid is used for the extraction of phytin instead of the usual HCl extraction. It is suggested that the modification introduced in this paper is more suitable for determining the distribution of the acid-soluble phosphorus compounds in foodstuffs.

During the course of our investigations on the distribution of phosphorus compounds in various cereals both in the resting seed and during germination, the method of McCance and Middowson (*Biochem. J.*, 1935, **29**, 2694) was followed for the estimation of phytin wherein $N/2$ HCl was used to extract the phytic acid. In order to obtain an accurate and strictly comparable data for the distribution of acid-soluble phosphorus compounds (*i.e.* labile phosphorus, total inorganic phosphorus, phytin phosphorus, etc.) it is necessary to carry out the estimations of all phosphorus compounds in the same extract, *i.e.*, in the trichloroacetic acid, which is generally employed for the extraction of acid-soluble phosphorus compounds except phytin. The present investigation was, therefore, undertaken with a view to finding out how far the values obtained by the trichloroacetic acid extraction method compare with those obtained by the usual HCl extraction method.

EXPERIMENTAL.

Powdered cereal (25 g.) was extracted first with 20 c.c of 10% trichloroacetic acid, in an ice-chest for about half an hour with occasional shaking and filtered, the filtrate being kept in the ice-chest. The sample was again extracted in the same manner with 20 c.c. of trichloroacetic acid and the filtrate from this was added to the first filtrate. The total extract was neutralised with $N/10$ -sodium hydroxide using phenolphthalein and again slightly acidified with $N/10$ -acid and the total volume was measured. 20 C.c. of this extract were taken and made up to 50 c.c. in a volumetric flask and 20 c.c. aliquots were taken for the estimation of phytin. The rest of the procedure followed was exactly the same as that of McCance and Middowson (*loc. cit.*).

Phytin Content of Cereals as determined by the HCl-extraction Method and Trichloroacetic Acid Method.

The following table gives the values of phytin estimated by the usual HCl-extraction method and by the trichloroacetic acid method.

TABLE I.

The phytin content of cereals.

| No. | HCl extraction method. | | | Trichloroacetic acid extraction method. | |
|---|------------------------|-----------|------------|---|------------|
| | Total P. | Phytin P. | Phytin P.* | Phytin P. | Phytin P.* |
| 1. Rice | 0.355% | 0.305% | 86 | 0.308% | 86.7 |
| 2. Rice germinated | 0.318 | 0.230 | 72.5 | 0.251 | 78.6 |
| 3. Rice (another sample) | — | 0.268 | — | 0.282 | — |
| 4. Ragi (<i>Eleusine coracana</i>) | — | 0.120 | — | 0.131 | — |
| 5. Bengal gram (<i>Cicer arietinum</i>) | — | 0.100 | — | 0.125 | — |
| 6. Green gram (<i>Phaseolus radiatus</i>) | 0.410 | 0.188 | 46 | 0.203 | 50.0 |
| 7. Green gram (germinated) | 0.540 | 0.161 | 30 | 0.185 | 34.3 |

* as % of total P.

The Influence of Concentration of Trichloroacetic Acid on the Extraction of Phytin.

The effect of varying concentrations of trichloroacetic acid on the extraction of phytin was then investigated. The results are presented in Table II.

TABLE II.

| <i>Rice.</i> | | |
|--------------|---|---------|
| Total P. | Concentration of trichloroacetic acid used. | Phytin. |
| 0.355% | 2% | 50% |
| " | 5 | 74 |
| " | 10 | 73.7 |

The results show that 5-10% trichloroacetic acid is the optimum concentration for the extraction of phytin.

The Influence of Repeated Extraction on the Phytin Content of the Extract.

In the following table are presented the results obtained on the influence of repeated extraction on the phytin content of the trichloroacetic acid extract.

TABLE III.

| <i>Rice.</i> | | |
|------------------|-----------------|-----------------|
| | 1st extraction. | 2nd extraction. |
| Total Phosphorus | Phytin P | Phytin P. |
| 0.355% | 0.277 | 0.006 |

The results show that practically the whole of phytin phosphorus is removed in the first extract. For all practical purposes, therefore, one extraction is enough to obtain the total quantity of phytin in the extract.

It is clear from the above results that the values obtained for the phytin content of cereals and pulses by the use of trichloroacetic acid as extractant compares favourably with those obtained by the HCl-extraction method. In some cases, however, slightly higher values were obtained by the trichloroacetic acid method which may be due to the efficient extraction of the phytin. It is suggested that trichloroacetic acid can replace HCl in the estimation of the phytin content of foodstuffs, particularly when the distribution of the acid-soluble phosphorus compounds in the same extract is to be determined.

My sincere thanks are due to Dr. K. V. Giri for suggesting the problem and for the guidance during the course of this investigation.

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STUDIES ON THE PHYSICO-CHEMICAL AND ELECTRO-KINETIC PROPERTIES OF GELS OF SILICIC ACID AND ALUMINIUM HYDROXIDE AND SOME SYNTHETIC AND NATURAL ALUMINOSILICATES, SPECIALLY IN RELATION TO ION-EXCHANGE PHENOMENA.

BY S. P. RAYCHAUDHURI AND A. K. M. QUDRAT GHANI.

In the present work the cation and anion exchange properties, buffer curve and electrokinetic properties of aluminosilicates of widely varying $\text{SiO}_2/\text{sesquioxide}$ ratios have been studied and these properties have been compared with similar properties of some naturally occurring aluminosilicates like kaolin, montmorillonite, halloysite, beidelite and limonite. Incidentally the co-precipitation of oppositely charged colloidal solutions was studied, by determining the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of different precipitates obtained by mixing the sols in varying proportions; the amount of free alumina on free silica given off by the different precipitates have also been studied.

Ghosh and Bhattacharyya (*Soil Sci.*, 1930, **29**, 311) have shown that mixed gels of silica and alumina and of silica and ferric oxide as obtained by mutual precipitation may have properties resembling in some respects those of the soil colloids, so far as adsorption of calcium and phosphate ions are concerned. Of the various investigations concerning the silica-sesquioxide ratio, reference may be made to those of Wiegner (*J. Soc. Chem. Ind.*, 1931, **50**, 31, 65), Mattson (*J. Agric. Res.*, 1926, **33**, 553; *First Internat. Cong. Soil Sci.*, 1926, II, 199), Anderson (*J. Agric. Res.*, 1929, **38**, 521), Bhattacharyya and Ganguli (*J. Indian Chem. Soc.*, 1936, **13**, 204, 213), Bhattacharyya (*ibid.*, 1937, **14**, 225) Sreenivasa (*Proc. Indian Acad. Sci.*, 1935, **1**, 607; **2**, 201; 1936, **3**, 283). Although considerable work has been done on synthetic aluminosilicates, no parallelism appears to have been drawn between synthetic and naturally occurring aluminosilicates of widely varying $\text{SiO}_2/\text{sesquioxide}$ ratios. Such a study was felt to be desirable.

In the present paper the base exchange properties including the buffer curves and electrokinetic properties of synthetic aluminosilicates of widely varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, obtained by mixing oppositely charged sols of SiO_2 and Al_2O_3 , have been compared with similar properties of naturally occurring clay minerals e.g. kaolin, bauxite, halloysite, limonite and montmorillonite.

E X P E R I M E N T A L.

Preparation of Sols.

Silicic Acid Sol.—Silicic acid sol was prepared by adding concentrated hydrochloric acid to a 20% solution of sodium silicate (Merck) and by subsequent dialysis

Aluminium Hydroxide Sol.—A solution of aluminium chloride containing 2.45% of Al_2O_3 was taken and ammonia added to it. The precipitate was well washed with hot water and then transferred to a flask containing water, the actual proportions being 1 litre of water for every 5 g. of Al_2O_3 . The whole was then heated and kept boiling, and 0.05N hydrochloric acid added from a burette. After each addition, water was added to replace that boiled off. An opalescent liquid that could be filtered unchanged was obtained. The colloidal solution of aluminium hydroxide, thus prepared, was then subjected to dialysis in a parchment bag for several days, the p_H at the stage when dialysis was discontinued being found to be 5.8.

Synthetic Aluminosilicate.—The synthetic aluminosilicates were prepared by mixing silicic acid sol and aluminium hydroxide sol in varying proportions. The precipitates formed were at first washed by ordinary dialysis in a parchment bag and subsequently by electrodialysis, until the anode was free of chlorine.

Electro-osmotic Experiment.

Electro-osmotic experiments with the precipitates were carried out by the modified method of Briggs, Bennet and Pierson (*J. Phys. Chem.*, 1918, **22**, 256). As recommended by Mukherjee (*Phil. Mag.*, 1922, **44**, 103; *Nature*, 1922, **110**, 732) and Mukherjee and Ray (*J. Indian Chem. Soc.*, 1924, **1**, 173) the straight tube was replaced by a U-tube, thus doing away with the use of porous plugs or glass-wool.

Determination of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the various precipitates.—The procedure followed was that given in A.O.A.C., 1938 Ed.

Determination of Base Exchange Capacities and of Buffer Curves.—The base exchange capacities and buffer curves of synthetic and natural aluminosilicates were determined by the method devised by Schofield (*J. Agric. Sci.*, 1933, **20**, 252), and followed by Raychaudhuri and Nandy-mazumdar (*Indian Soc. Soil Sci.*, 1939, **2**, 34; *Indian J. Agric. Sci.*, 1940, **10**, 62), Raychaudhuri, Sulaiman and Basuraychaudhuri, *ibid.*, 1941, **11**, 603), and Raychaudhuri and Basuraychaudhuri (*ibid.*, 1942, **12**, 137).

Determination of the Cataphoretic Speeds of Kaolin.—The cataphoretic speeds of kaolin were determined by means of the cataphoretic cell of

Freundlich and Abramson (*Z. physikal. Chem.*, 1927, **128**, 25; 1928, **133**, 57; cf. also Northrup, *J. Gen. Physiol.*, 1922, **4**, 629 and Brown and Brown, *Brit. J. Expt. Path.*, 1929, **10**, 61). The cataphoretic velocities of the particles at depths $\frac{1}{2}D$ and $\frac{4}{5}D$ were measured, the mean value being taken (cf. Smoluchowski, Graetz, "Handbuch der Elektrizität und Magnetismus," 1914, **II**, 306).

Determination of Free Silica and Free Alumina in the Synthetic Aluminosilicates.—The quantities of free silica and free alumina in the synthetic aluminosilicates were determined by following essentially the method of Drosdoff and Truog (*J. Amer. Soc. Agron.*, 1935, **27**, 312).

Preparation of Aluminosilicates free of Alumina.—Following the procedure of Mattson (*Soil. Sci.*, 1931, **31**, 311) the precipitates of silica, alumina and aluminosilicates were treated with a hot 10% solution of aluminium chloride to get rid of free alumina.

RESULTS AND DISCUSSION.

Compositions of Silicic Acid and Aluminium Hydroxide Sols and of Precipitated Gels.

- (i) Conc. of silic acid sol—1 mol of SiO_2 in 1164 c.c. of sol.
- (ii) Conc. of aluminium hydroxide sol—1 mol. of Al_2O_3 in 4548 c.c. of sol.
- (iii) Compositions of precipitated gels are shown in Table I.

TABLE I.

| | | | | | | | |
|---|------|------|-----|-----|-----|------|------------------|
| Mixing ratios of sols... ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | 0.5 | 1.0 | 2.0 | 4.0 | 8.0 | 25.0 | Silicic acid gel |
| Comp. ratios of the gels... ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | 0.44 | 0.98 | 2.0 | 3.0 | 7.0 | 16.0 | |

In order to examine whether a precipitated mass can combine with silica on long standing, two types of silicic acid sols (dialysed for 3 and 4 days respectively) were mixed with a sample of alumina sol and the resulting precipitate was analysed after 5, 10 and 60 hours after mixing the sols. The results are shown in Table II.

TABLE II.

| $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mixing ratio=2) after mixing Al_2O_3 sol with SiO_2 sol. after | | | | |
|---|-------|--------|---------|--------|
| Silicic acid sol dialysed for | 1 hr. | 5 hrs. | 10 hrs. | 60 hrs |
| 3 days | ... | 1.78 | 1.78 | 1.78 |
| 4 | 0.3 | 1.20 | 1.35 | 1.78 |

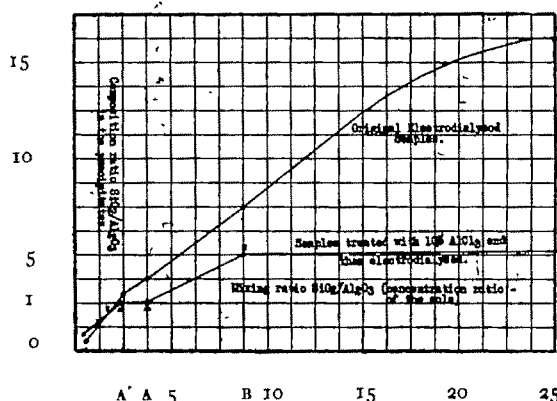
The sol dialysed for 4 days was acid-free and almost a gel. This experiment tends to show that aluminium can combine with silica even after lump formation.

The compositions of the residues after treatment with hot AlCl_3 solutions are shown in Table III and plotted graphically in Fig. 1.

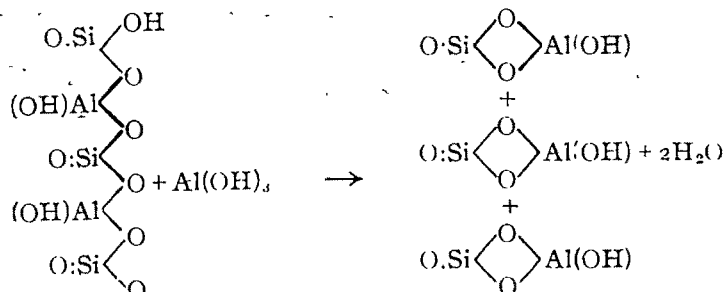
TABLE III.

| | | | | | | |
|--|------|------|------|------|------|------|
| Mixing ratios of sols ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | 0.5 | 1.0 | 2.0 | 4.0 | 8.0 | 25.0 |
| Comp. ratios of the gels (, ,) | 0.67 | 1.21 | 1.78 | 1.78 | 4.96 | 5.41 |

FIG. 1.



In Fig. 1 from point I to A, the Al added gets combined with the compound having $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio=3 and as this compound exists in increasing amount from I to A, the amount of aluminosilicate that gets combined with Al increases in the same manner, so that eventually we get a straight line for this portion of the curve; the combination may be represented as:



From the point A to B the combination of Al with the aluminosilicate gets lesser due the fact that above the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio=3, the complex gets

covered with free SiO_2 , resulting in a gradual retardation of the above reaction, because the alumina cannot get to the compound due to intervention of silica. That Al can combine with gellified Al-silicates is brought out in Table III.

From B. onwards we again find a straight line. This we have tried to explain by assuming that at B the micelles get completely covered with free SiO_2 , and no chemical combination can henceforth take place; on treatment with AlCl_3 the aluminium added merely gets adsorbed on the previously adsorbed silica. Though this process of adsorption begins from A, and the slope AB is in part due to this effect, at B a maximum is reached, and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio remains steady near about 5. A further confirmation of the above theory presents itself when the electrokinetic and base-exchange properties of the compounds at A and A' are compared. Such a comparison tends to show that the samples A and A' are more or less alike. The millimols of silica and alumina per 100 g. of precipitated gels (oven dry basis) before and after treatment with a hot 10% solution of aluminium chloride were determined by treating these gels with a 2% solution of sodium carbonate at 70° for 10 hours (Drosdoff and Truog, *loc. cit.*) The results are shown in Table IV.

TABLE IV.

| A. Before treatment with 10% AlCl_3 | | | B. After treatment with 10% AlCl_3 | | |
|--|--|---------------------------|---|--|---------------------------|
| Comp. ratio. | M. mols after treatment with 2% Na_2CO_3 soln. | | Comp. ratio. | M. mols after treatment with 2% Na_2CO_3 soln. | |
| $\text{SiO}_2/\text{Al}_2\text{O}_3$. | SiO_2 | Al_2O_3 . | $\text{SiO}_2/\text{Al}_2\text{O}_3$. | SiO_2 . | Al_2O_3 . |
| 0.44 | Nil | 257.4 | 0.67 | Nil | 85.2 |
| 0.98 | " | 104.3 | 1.21 | " | 26.3 |
| 2.00 | 61.6 | Nil | 1.78 | 22.1 | 63.4 |
| 3.00 | 85.4 | " | 1.78 | 24.3 | 65.1 |
| 7.00 | 163.3 | " | 4.96 | 88.3 | 197.6 |
| 16.00 | 455.9 | " | 5.41 | 210.7 | 276.2 |

We find from Table IV A that at lower ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the original precipitates, only free Al_2O_3 is given off, whereas at higher ratios SiO_2 alone is given off and in increasing quantities. Results in Table IV (A & B) show that in precipitates, where $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is below 1.21 (*i.e.* where treatment with 10% hot AlCl_3 has resulted in peptisation of some free alumina), the quantity of alumina extracted with 2% Na_2CO_3 solution is less in the precipitated gels after treatment with hot AlCl_3 solution than before. Thus where the mixing ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 0.5 (*vide* Table I) the extracted alumina in millimols per 100 g. of gel reduces from 257.4 to 85.2. Also where

the mixing ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 1.00, this figure reduces to 26.3. Beyond this mixing ratio, however, treatment with 10% AlCl_3 has resulted in positive adsorption of alumina and we find that increasing quantities of alumina are being given off. Table IV also shows that the quantities of SiO_2 given off by treatment with 2% Na_2CO_3 solution becomes less after treatment with hot 10% AlCl_3 solution and in both cases SiO_2 given off increases as we pass down the column. This relative decrease of free SiO_2 (extracted with 2% Na_2CO_3 solution) and the increase in free Al_2O_3 extracted by the same process, after treatment of the precipitated gels with hot 10% AlCl_3 solution, explains the increase in positive charge after treatment of the precipitates with hot 10% AlCl_3 solution (*vide* Table V). It would be interesting to consider this decrease in the quantities of free SiO_2 (Tables IV and V) in the light of the postulations regarding the structure of these aluminium silicates given before. It has been already assumed that at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, much SiO_2 remains free imparting to the precipitate a negative charge (Table V). On treatment with hot AlCl_3 solution, three definite processes occur in successive stages (Fig. 11). At first there is a decrease in the alumina content of the precipitate and the quantity of free alumina decreases. Then in the second stage, treatment with hot AlCl_3 results in the combination of aluminium and the aluminium content of the precipitate increases and consequently the free alumina given off increases from 0 to 63.4 and 65.1. The quantity of free SiO_2 given off naturally decreases as most of it has combined with the aluminium. The charge is positive (*vide* Table V) as there is more of free alumina than free SiO_2 . Then in the third stage, aluminium is mostly adsorbed on the precipitate and some of it of course combines chemically with the SiO_2 . The result is that the quantity of free SiO_2 decreases after treatment with hot AlCl_3 and the quantity of free alumina given off greatly increases from 0 to 197.1 and 276.2, the charge becoming positive (*vide* Table V). Another interesting point in Table IV is that as we go down the column we find the quantity of free SiO_2 given off increases but the quantity of free alumina given off at first decreases from 85.2 to 26.3 and then increases from 63.4 to 276.2.

Electro-osmotic Experiments with Synthetic Gels of Aluminosilicates and with Silicic Acid Gel.

Table V shows the electro-osmotic movement in cm. per 5 mins. with the electrodialysed precipitated gels of aluminosilicates (Table VA) and with the same gels after treatment with a hot 10% solution of aluminium chloride (Table VB).

TABLE V.

| A. Electrolysed precipitated gels of aluminosilicates | | | B. Electrolysed pptd. gels after treatment with hot 10% AlCl_3 and subsequently electrolysed. | |
|---|--|--|--|--|
| Mixing ratio of sols ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | Comp. ratio of ppt. ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | Electro-osmotic movement (cm / 5 min.) | Comp ratio of ppt. ($\text{SiO}_2/\text{Al}_2\text{O}_3$) | Electro-osmotic movement (cm / 5 min.) |
| 0.50 | 0.44 | +2.9 | 0.67 | +2.5 |
| 1.00 | 0.98 | +1.0 | 1.12 | +0.3 |
| 2.00 | 2.00 | -1.6 | 1.78 | +2.0 |
| 4.00 | 3.00 | -2.3 | 1.78 | +2.0 |
| 8.00 | 7.00 | -2.5 | 4.96 | +3.3 |
| 25.00 | 16.00 | -4.8 | 5.41 | +4.1 |
| Silicic acid gel | ... | -5.9 | | |

That in presence of AlCl_3 a reversal of charge might be effected is shown from the following data taken from Mattson (*loc. cit.*).

TABLE VI.

Electrolysed Sharkey soil

(0.2 g. colloid per litre).

| | | | | | | | |
|---|-----|------|-------|-------|------------|-------|-------|
| AlCl_3 (m. equivalent/litre) | .. | 0.0 | 0.2 | 1.0 | 1.5 | 2.0 | 4.0 |
| $\mu/\text{sec.}/\text{volt}/\text{cm}$ | ... | -3.2 | -0.80 | -0.17 | ± 0.00 | +0.14 | +0.49 |

Mattson has explained this reversal in charge by assuming the formation of compounds like oxychlorides, which dissociate into diffusible anions and an electropositive colloidal complex:

Electro-osmotic Experiments with Synthetic Gels of Aluminosilicates and with Silicic Acid Gel.

In the following tables (VII-XIX) I_{MCl} represents the electro-osmotic movement of bubble for 5 min. in cm. for a salt MCl and I_{LiCl} represents similar movement for the salt LiCl . We may assume the intensity of adsorption to be proportional to the cataphoretic speed. The third column gives the value of $I_{\text{MCl}}/I_{\text{LiCl}}$. If we take I_{Li} to be zero, this reduces to I_{M} , thus giving the intensity of adsorption for a cation M relative to Li . Li is chosen due to the fact that among the cations taken, it has the weakest exchange intensity. Similarly the sixth

column of the tables $I_A = I_{NO_3}$ represents the intensity for an anion $A(I_A)$. It may be pointed out that I_M is throughout positive and I_A is throughout negative. The strengths of various electrolytic solutions used are $N/500$ in all the cases. Electro-osmotic movement is expressed in cm./5 min.

Tables VII to XIII give data for gels untreated with hot 10% $AlCl_3$ solution, whilst Tables XIV to XIX give data for gels treated with hot 10% $AlCl_3$ solution.

TABLE VII.

SiO_2/Al_2O_3 mixing ratio = 0.50.

„ composition „ = 0.44.

| Salt used. | Movement. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement. | $I_{KA} - I_{KNO_3} = I_A$ |
|------------|-----------|----------------------------|---------------|-----------|----------------------------|
| LiCl | +4.20 | — | $K_4Fe(CN)_6$ | -0.6 | -7.10 |
| NaCl | +4.3 | 0.1 | K_2HPO_4 | ± 0.0 | -6.5 |
| KCl | +4.4 | 0.2 | K_2SO_4 | +2.4 | -4.1 |
| $MgCl_2$ | +4.4 | 0.2 | KCl | +4.4 | -2.1 |
| $CaCl_2$ | +4.5 | 0.3 | KI | +4.9 | -1.6 |
| $BaCl_2$ | +4.5 | 0.3 | KBr | +6.0 | -0.5 |
| $AlCl_3$ | +4.7 | 0.5 | KNO_3 | +6.5 | — |
| Water | +2.9 | — | — | — | — |

TABLE VIII.

SiO_2/Al_2O_3 mixing ratio = 1.00.

„ composition „ = 0.98.

| Salt used | Movement. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement | $I_{KA} - I_{KNO_3} = I_A$ |
|-----------|-----------|----------------------------|---------------|-----------|----------------------------|
| LiCl | +1.7 | — | $K_4Fe(CN)_6$ | -0.5 | -3.0 |
| NaCl | +1.9 | +0.2 | K_2HPO_4 | ± 0.0 | -2.5 |
| KCl | +2.0 | +0.3 | K_2SO_4 | +0.7 | -1.8 |
| $MgCl_2$ | +2.2 | +0.5 | KCl | +2.0 | -0.5 |
| $CaCl_2$ | +2.3 | +0.6 | KI | +2.0 | -0.5 |
| $BaCl_2$ | +2.5 | +0.8 | KBr | +2.3 | -0.2 |
| $AlCl_3$ | +2.7 | +1.0 | KNO_3 | +2.5 | — |
| Water | +1.0 | — | — | — | — |

TABLE IX.

SiO₂/Al₂O₃ mixing ratio = 2.00

,, composition ,, = 2.00

| Salt used. | Movement. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used | Movement. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|-----------|----------------------------|------------------------------------|-----------|----------------------------|
| LiCl | -3.4 | — | K ₄ Fe(CN) ₆ | -3.8 | -1.0 |
| NaCl | -3.1 | +0.3 | K ₂ HPO ₄ | -3.5 | -0.7 |
| KCl | -2.9 | +0.5 | KI | -3.2 | -0.4 |
| MgCl ₂ | -2.6 | +0.8 | K ₂ SO ₄ | -3.2 | -0.4 |
| CaCl ₂ | -2.4 | +1.0 | KBr | -3.0 | -0.2 |
| BaCl ₂ | -2.2 | +1.2 | KCl | -2.9 | -0.1 |
| AlCl ₃ | -1.8 | +1.6 | KNO ₃ | -2.8 | — |
| Water | -1.6 | — | — | — | — |

TABLE X.

SiO₂/Al₂O₃ mixing ratio = 4.00

,, composition ,, = 3.00

| Salt used. | Movement. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|-----------|----------------------------|------------------------------------|-----------|----------------------------|
| LiCl | -5.7 | — | K ₄ Fe(CN) ₆ | -4.8 | -0.4 |
| NaCl | -4.8 | +0.9 | K ₂ HPO ₄ | -4.7 | -0.3 |
| KCl | -4.4 | +1.3 | KI | -4.6 | -0.2 |
| MgCl ₂ | -3.9 | +1.8 | K ₂ SO ₄ | -4.6 | -0.2 |
| CaCl ₂ | -3.5 | +2.2 | KBr | -4.5 | -0.1 |
| BaCl ₂ | -3.1 | +2.6 | KCl | -4.4 | 0.0 |
| AlCl ₃ | -2.6 | +3.1 | KNO ₃ | -4.4 | — |
| Water | -2.3 | — | — | — | — |

TABLE XI.

SiO₂/Al₂O₃ mixing ratio = 8.0.

,, composition ,, = 7.0.

| Salt used. | Movement | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|----------|----------------------------|------------------------------------|-----------|----------------------------|
| LiCl | -8.0 | — | K ₄ Fe(CN) ₆ | -7.2 | -0.3 |
| NaCl | -7.3 | +0.7 | K ₂ HPO ₄ | -7.2 | -0.3 |
| KCl | -7.0 | +1.0 | KI | -7.1 | -0.2 |
| MgCl ₂ | -5.8 | +2.2 | K ₂ SO ₄ | -7.1 | -0.2 |
| CaCl ₂ | -4.9 | +3.1 | KBr | -7.0 | -0.1 |
| BaCl ₂ | -4.1 | +3.9 | KCl | -6.9 | 0.0 |
| AlCl ₃ | -3.1 | +4.9 | KNO ₃ | -6.9 | — |
| Water | -2.5 | — | — | — | — |

TABLE XII.

SiO₂/Al₂O₃ mixing ratio = 25%.

,, composition ,, = 16%.

| Salt used | Movement in 1 min. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement in 1 min. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|-----------------------|----------------------------|------------------------------------|-----------------------|----------------------------|
| LiCl | -6.2 | — | K ₄ Fe(CN) ₆ | -6.3 | -0.2 |
| NaCl | -6.1 | +0.1 | K ₂ HPO ₄ | -6.2 | -0.1 |
| KCl | -6.1 | +0.1 | KI | -6.1 | 0.0 |
| MgCl ₂ | -5.9 | +0.5 | K ₂ SO ₄ | -6.1 | 0.0 |
| CaCl ₂ | -5.6 | +0.6 | KBr | -6.1 | 0.0 |
| BaCl ₂ | -5.4 | +0.8 | KCl | -6.1 | 0.0 |
| AlCl ₃ | -5.0 | +1.2 | KNO ₃ | -6.1 | — |
| Water | -4.8 | — | — | — | — |

TABLE XIII.

Silicic acid gel.

| Salt used | Movement in 1 min. | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement in 1 min. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|-----------------------|----------------------------|------------------------------------|-----------------------|----------------------------|
| LiCl | -6.2 | — | K ₄ Fe(CN) ₆ | -6.2 | 0.0 |
| NaCl | -6.2 | 0.0 | K ₂ HPO ₄ | -6.2 | 0.0 |
| KCl | -6.2 | 0.0 | KI | -6.2 | 0.0 |
| MgCl ₂ | -6.1 | -0.1 | K ₂ SO ₄ | -6.2 | 0.0 |
| CaCl ₂ | -6.1 | -0.1 | KBr | -6.2 | 0.0 |
| BaCl ₂ | -6.1 | -0.1 | KCl | -6.2 | 0.0 |
| AlCl ₃ | -6.0 | -0.2 | KNO ₃ | -6.2 | 0.0 |
| Water | -5.9 | — | — | — | — |

TABLE XIV.

SiO₂/Al₂O₃ mixing ratio = 0.50.

,, composition ,, = 0.67.

| Salt used. | Movement | $I_{MCl} - I_{LiCl} = I_M$ | Salt used. | Movement. | $I_{KA} - I_{KNO_3} = I_A$ |
|-------------------|----------|----------------------------|------------------------------------|-----------|----------------------------|
| LiCl | +1.3 | — | K ₄ Fe(CN) ₆ | -0.1 | -2.7 |
| NaCl | +1.4 | +0.1 | K ₂ HPO ₄ | +0.4 | -2.2 |
| KCl | +1.5 | +0.2 | K ₂ SO ₄ | +1.0 | -1.6 |
| MgCl ₂ | +1.7 | +0.4 | KCl | +1.5 | -1.1 |
| CaCl ₂ | +1.8 | +0.5 | KI | +2.0 | -0.6 |
| BaCl ₂ | +1.9 | +0.6 | KBr | +2.3 | -0.3 |
| AlCl ₃ | +2.1 | +0.8 | KNO ₃ | +2.6 | — |
| Water | +2.5 | — | — | — | — |

TABLE XV.

SiO₂/Al₂O₃ mixing ratio=1'0.

,, composition ,, =1'12.

| Salt used. | Movement. | $I_{MCl}-I_{LiCl}=I_M$ | Salt used. | Movement. | $I_{KA}-I_{KNO_3}=I_A$ |
|-------------------|-----------|------------------------|------------------------------------|-----------|------------------------|
| LiCl | +1'8 | — | K ₄ Fe(CN) ₆ | -0'3 | -3'1 |
| NaCl | +2'0 | +0'2 | K ₂ HPO ₄ | +1'5 | -1'3 |
| KCl | +2'3 | +0'5 | K ₂ SO ₄ | +2'0 | -0'8 |
| MgCl ₂ | +2'4 | +0'6 | KCl | +2'3 | -0'5 |
| CaCl ₂ | +2'5 | +0'7 | KI | +2'5 | -0'3 |
| BaCl ₂ | +2'6 | +0'8 | KBr | +2'6 | -0'2 |
| AlCl ₃ | +2'9 | +1'1 | KNO ₃ | +2'8 | — |
| Water | +2'5 | — | — | — | — |

TABLE XVI.

SiO₂/Al₂O₃ mixing ratio=2'00.

,, composition ,, =1'78.

| Salt used. | Movement. | $I_{MCl}-I_{LiCl}=I_M$ | Salt used. | Movement. | $I_{KA}-I_{KNO_3}=I_A$ |
|-------------------|-----------|------------------------|------------------------------------|-----------|------------------------|
| LiCl | +1'9 | — | K ₄ Fe(CN) ₆ | -0'5 | -3'9 |
| NaCl | +2'2 | +0'3 | K ₂ HPO ₄ | +1'5 | -1'9 |
| KCl | +2'4 | +0'5 | K ₂ SO ₄ | +2'0 | -1'4 |
| MgCl ₂ | +2'7 | +0'8 | KCl | +2'4 | -1'0 |
| CaCl ₂ | +2'9 | +1'0 | KI | +2'7 | -0'7 |
| BaCl ₂ | +3'1 | +1'2 | KBr | +3'0 | -0'4 |
| AlCl ₃ | +3'3 | +1'4 | KNO ₃ | +3'4 | — |
| Water | +2'0 | — | — | — | — |

TABLE XVII.

SiO₂/Al₂O₃ mixing ratio=4'00.

,, composition ,, =1'78.

| Salt used. | Movement. | $I_{MCl}-I_{LiCl}=I_M$ | Salt used. | Movement. | $I_{KA}-I_{KNO_3}=I_A$ |
|-------------------|-----------|------------------------|------------------------------------|-----------|------------------------|
| LiCl | +1'9 | — | K ₄ Fe(CN) ₆ | -0'5 | -4'0 |
| NaCl | +2'2 | +0'3 | K ₂ HPO ₄ | +1'5 | -2'0 |
| KCl | +2'4 | +0'5 | K ₂ SO ₄ | +2'0 | -1'5 |
| MgCl ₂ | +2'7 | +0'8 | KCl | +2'4 | -1'1 |
| CaCl ₂ | +3'0 | +1'1 | KI | +2'7 | -0'8 |
| BaCl ₂ | +3'1 | +1'2 | KBr | +3'0 | -0'5 |
| AlCl ₃ | +3'3 | +1'4 | KNO ₃ | +3'5 | — |
| Water | +2'0 | — | — | — | — |

TABLE XVIII.

SiO₂/Al₂O₃ mixing ratio=8'00.

,, composition ,, =4'96.

| Salt used. | Movement. | $I_{\text{NaCl}} - I_{\text{LiCl}} = I_M$ | Salt used. | Movement. | $I_{\text{KCl}} - I_{\text{KNO}_3} = I_A$ |
|-------------------|-----------|---|---------------------------------|-----------|---|
| LiCl | +1'9 | — | KFe(CN) ₆ | +0'1 | -3'7 |
| NaCl | +2'4 | +0'5 | K ₂ HPO ₄ | +1'3 | -2'5 |
| KCl | +2'5 | +0'6 | K ₂ SO ₄ | +2'0 | -1'8 |
| MgCl ₂ | +2'9 | +1'0 | KCl | +2'5 | -1'3 |
| CaCl ₂ | +3'1 | +1'2 | KI | +3'0 | -0'8 |
| BaCl ₂ | +3'3 | +1'4 | KBr | +3'4 | -0'4 |
| AlCl ₃ | +3'6 | +1'7 | KNO ₃ | +3'8 | — |
| Water | +3'0 | — | — | — | — |

TABLE XIX.

SiO₂/Al₂O₃ mixing ratio=25'00.

,, composition ,, =5'41.

| Salt used | Movement. | $I_{\text{NaCl}} - I_{\text{LiCl}} = I_M$ | Salt used. | Movement. | $I_{\text{KCl}} - I_{\text{KNO}_3} = I_A$ |
|-------------------|-----------|---|------------------------------------|-----------|---|
| LiCl | +2'1 | — | K ₄ Fe(CN) ₆ | +0'3 | -4'0 |
| NaCl | +2'6 | +0'5 | K ₂ HPO ₄ | +1'4 | -2'9 |
| KCl | +3'0 | +0'9 | K ₂ SO ₄ | +2'4 | -1'9 |
| MgCl ₂ | +3'4 | +1'3 | KCl | +3'0 | -1'3 |
| CaCl ₂ | +3'8 | +1'7 | KI | +3'5 | -0'8 |
| BaCl ₂ | +4'1 | +2'0 | KBr | +3'9 | -0'4 |
| AlCl ₃ | +4'5 | +2'4 | KNO ₃ | +4'3 | — |
| Water | +4'1 | — | — | — | — |

TABLE XX.

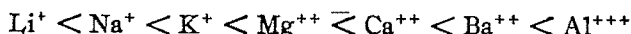
*Cataphoretic experiments with kaolin by Freundlich and
Abramson's cell.*

| Salt used (N/500). | μ /sec/ volt/cm. | Salt used (N/500). | μ /sec/ volt/cm. | Salt used (N/500). | μ /sec/ volt/cm. | Salt used (N/500). | μ /sec/ volt/cm. |
|-----------------------|-------------------------|------------------------------------|-------------------------|-----------------------|-------------------------|-----------------------|-------------------------|
| LiCl | -1'33 | K ₄ Fe(CN) ₆ | -1'12 | CaCl ₂ | -0'59 | KBr | -0'78 |
| NaCl | -0'91 | K ₂ HPO ₄ | +1'11 | BaCl ₂ | -0'53 | KCl | -0'76 |
| KCl | -0'76 | KI | -0'80 | AlCl ₃ | -0'42 | KNO ₃ | -0'74 |
| MgCl ₂ | -0'67 | K ₂ SO ₄ | -0'79 | Water | -0'34 | — | — |

It will be found in Tables VII to XX that in general the difference of velocity from Ba⁺⁺ to Al⁺⁺⁺ is greater than any other difference and the

value for Al^{+++} more nearly approaches that for H^+ (the electro dialysed sample). This is explained by the fact that Al^{+++} being a constituent ion fits in the general structure of the gel, and comes into closer contact with the nuclear structure. The works of Mukherjee and Fajans have shown that even gels may possess regular patterns like crystals (*cf.* Fajans and Backerath, *Z. physikal. Chem.*, 1921, 97, 478; Mukherjee and Ray, *J. Indian Chem. Soc.*, 1924, 1, 173).

The results of these investigations show that the intensity of cation adsorption follows more or less the Hoffmeister series,



It might be that besides the thickness of the double layer (*d*) other factors might come into play, *e.g.*, the comparative dissociation of the ions entering and leaving, which amongst others modifies the cataphoretic speed and this dissociation decreases from Na^+ to Ca^{++} or Ba^{++} . There can be simultaneous anion and cation adsorption and that the migration micelles rather than being a definite measure of the intensity of adsorption is dependent on other factors as well, the chief among them being the dissociation of complex formed by molecular adsorption, the hydration and the kinetic energy of the ions (*cf.* Mukherjee, *Trans. Faraday Soc.*, 1921, 16, 103). When these factors are allowed, especially the relative dissociation, we can get a comparative study of the intensity of adsorption. Thus we find that in general the order is $Fe(CN)_6^{IV} > HPO_4^{''} > SO_4^{''} > Br' > Cl' > NO_3'$. This more or less follows the lyotropic series which is $I' > Br' > Cl' > NO_3' > SO_4^{''}$. Though the position of $SO_4^{''}$ in the lyotropic series happens to be the last; $SO_4^{''}$ from H_2SO_4 has been known to be more strongly adsorbed in soil than Cl' , the order being $PO_4^{'''} > SO_4^{''} > Cl'$ (Mattson, 1929). This may be explained as being due to the presence of free sesquioxides in the samples.

With positively charged precipitates (Tables XIV to XIX) the positive charge decreases in the following order: $Al^{+++} > Ba^{++} > Ca^{++} > Mg^{++} > K^+ > Na^+ > Li^+$. The behaviour of anions shows that the positive charge diminishes in the following order: $NO_3' > Br' > I' > Cl' > SO_4^{''} > PO_4^{'''}$ > $Fe(CN)_6^{IV}$. With positively charged precipitate the charge is throughout negative in presence of $Fe(CN)_6^{III}$. This reversal of charge can be explained from Mukherjee's point of view (*loc. cit.*) as being due to the adsorption of the highly negatively charged $Fe(CN)_6^{III}$ ions in the primary sheet of the double layer. The latter imparts a negative charge to the whole particle. Our findings are that $Fe(CN)_6^{III}$ in all cases

decreases the positive charge to a large extent, though an actual reversal of sign may not occur when the initial charge is highly positive.

FIG. 2.

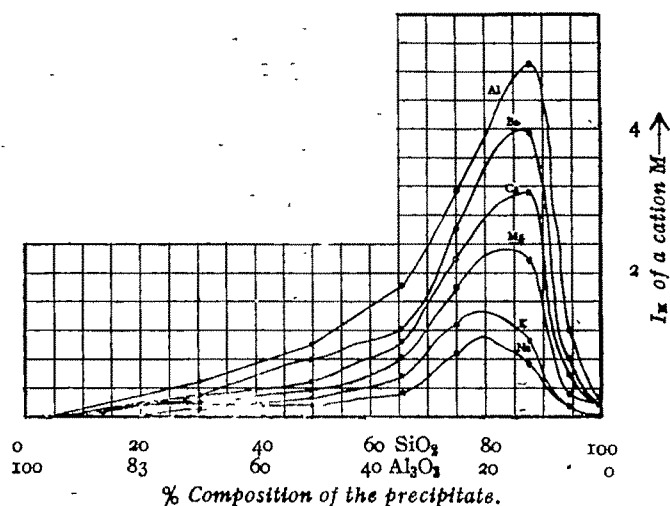
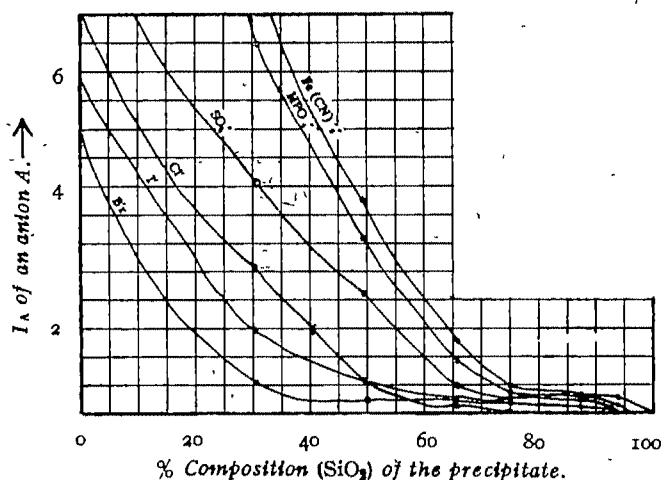


FIG. 3.

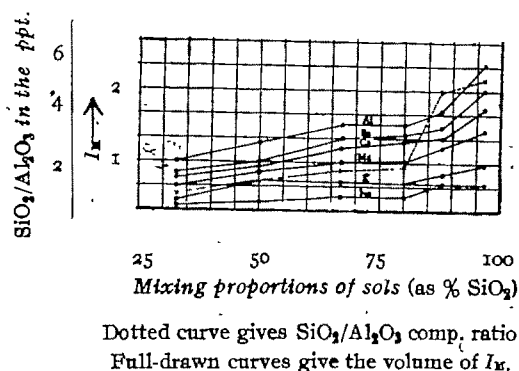


The results in Tables VII to XX have been plotted graphically in Figs. 2, 3, 4 and 5. Fig. 2 shows the value of I_M (intensity of adsorption of the cations relative to Li when the value for Li is taken to be zero) plotted against the percentage composition of the different precipitates (untreated with 10% hot AlCl_3). The curves show peaks, proving that at a region where the SiO_2 is 80-90%, the cation adsorption is maximum.

This is in accordance with the current views that at a particular $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio the cation adsorption is maximum (*cf.* Weigner, *loc. cit.*) Fig. 3 gives the value of I_a (intensity of adsorption of the anions relative to NO_3 when the value for NO_3 is taken to be zero) plotted against the percentage composition of the precipitates. The curves show that the anion adsorption drops down with the SiO_2 content of the precipitates, pure SiO_2 gel showing zero intensity. This corroborates the suggestion of Mattson (*J. Agric. Res.*, 1926, 38, 553) that the adsorption of anions in soils is largely due to free sesquioxide. Bhattacharya and Ganguly (*loc. cit.*) have found a similar set of curves using a different method.

In Fig. 4 have been plotted the I_a values for gels treated with 10% AlCl_3 not against the percentage composition (some of the samples giving the same percentage composition, this method was not resorted to) but against the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixing ratio of the sols when the precipitates were being formed. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ composition ratio curve was next superimposed and it was found that within moderate limits (here less than 5.41 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio values) the intensity curve follows the composition ratio curve, *i.e.* within moderate limits of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio values, the intensity of cation adsorption increases with SiO_2 content.

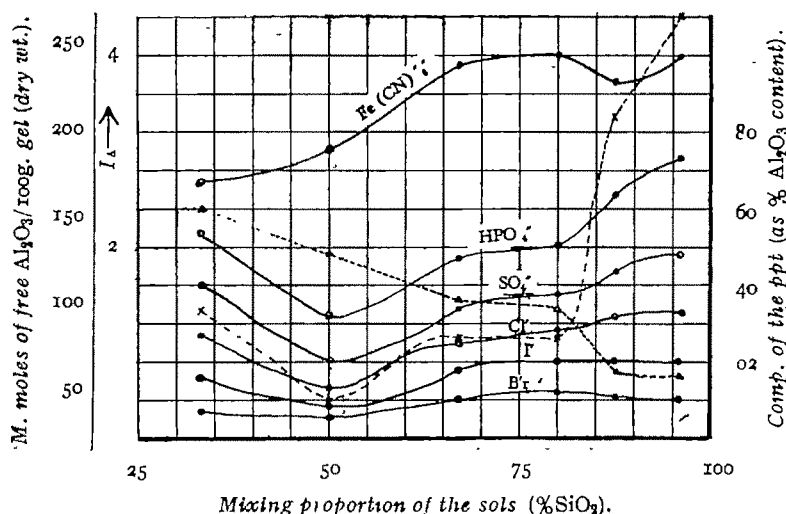
FIG. 4.



In Fig. 5 similarly have been plotted I_a values for gels treated with 10% hot AlCl_3 solution, not against percentage composition, but have later been superimposed on the composition ratio curve and the curve for free alumina content (*i.e.* the Al_2O_3 which is liberated on treatment with 2% Na_2CO_3 , *cf.* Table II). Here we find that the intensity curves follow this latter curve, thus again showing that anion adsorption is connected with free sesquioxide content and not with the total sesquioxide content. $\text{Fe}(\text{CN})_6^{IV}$ does not give a minimum. Our findings are that this ion, in

all cases, decreases the positive charge though a reversal may occur only when the initial positive charge is rather weak. It may be mentioned

FIG. 5.



Dotted curve gives the comp. of the ppt. (% of total Al_2O_3).
Full-drawn curves give I_A and broken curves give free Al_2O_3 content.

that I_A includes the charge of the colloid, and this latter depends on the initial positive charge of the particle and on the amount of ion adsorbed. Both these factors increase with the increase of free alumina, but while the effect of the former is to increase the positive charge, that of the latter is to decrease it and I_A will merely give the relative difference of the two opposite process. In the case of $\text{Fe}(\text{CN})_6^{4-}$, during the first part of curve (left side) the former effect is stronger i.e. the particle becomes initially relatively less positively charged due to less of free alumina as compared with the loss in negative charge due to less of $\text{Fe}(\text{CN})_6^{4-}$ being adsorbed.

Table XX shows the variation of electrical charge of electrodialysed kaolin with different anions and cations. The results show that the adsorption of cations follows the Hoffmeister's series, viz., $\text{Al}^{+++} > \text{Ba}^{++} > \text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Also the adsorption of anions follows the order, $\text{Fe}(\text{CN})_6^{4-} > \text{HPO}_4^{2-} > \text{I}^- > \text{SO}_4^{2-} > \text{Br}^- > \text{Cl}^- > \text{NO}_3^-$. These orders of cationic and anionic adsorptions are similar to those found for the negatively charged gels and are in complete agreement with the theories of ion adsorption put forward by Mukherjee, (*loc. cit.*).

Determination of Buffer Curves.

The results are shown in Tables XXI, XXII and XXIII. The corresponding buffer curves have been drawn in Figs. 6, 7 and 8.

TABLE XXI.

Base-uptake per 100 g. original in m. equivalents electrolysed precipitated gels (oven-dry basis).

| p_H . | SiO_2 . | Ratio of SiO_2 to Al_2O_3 equals to | | | | | Al_2O_3 . |
|---------|-----------|---|--------|--------|--------|-----------|-------------|
| | | 1. | 2. | 4. | 8. | 25 | |
| 1'3 | -11'3 | -72'5 | -87'5 | -60'0 | -42'5 | -35'0 | +1'8 |
| 2'9 | -16'5 | -87'0 | -77'5 | -55'1 | -30'1 | -27'1 | +2'2 |
| 4'6 | +1'0 | -30'0 | -39'1 | -23'7 | -9'8 | \pm 0'0 | +6'8 |
| 7'1 | +1'5 | +125'0 | +140'0 | +180'1 | +192'7 | +120'1 | +12'8 |
| 9'8 | +17'1 | +187'5 | +179'0 | +226'3 | +237'5 | +193'7 | +107'2 |
| 12'5 | +37'0 | +207'5 | +190'0 | +247'5 | +262'6 | +237'6 | +149'0 |

TABLE XXII.

Base-uptake in milliequivalents per 100 g. of precipitated and electrolysed gels after treatment with 10% hot $AlCl_3$ solution and subsequent electrodialysis (oven-dry basis).

| p_H | Ratio of SiO_2 to Al_2O_3 equals to | | | | |
|-------|---|--------|--------|--------|--------|
| | 1. | 2. | 4. | 8 | 25. |
| 1'3 | -52'5 | -20'1 | -9'0 | -32'3 | -4'9 |
| 2'9 | -63'2 | -29'7 | -13'1 | -37'5 | -7'6 |
| 4'6 | +17'5 | -2'1 | +12'5 | +72'5 | +224'9 |
| 7'1 | +48'0 | +181'5 | +267'6 | +213'7 | +426'9 |
| 9'8 | +54'5 | +267'5 | +320 | +297'4 | +470'2 |
| 12'5 | +57'5 | +310 | +337'6 | +350 | +491'8 |

TABLE XXIII. *

Base-uptake per 100 g. of electrolysed kaolin (oven-dry basis).

| Minerals. | $p_H \rightarrow$ 1'3 | 2'9 | 4'6 | 7'1 | 9'8 | 12'5 |
|-----------------|-----------------------|-------|-------|-------|-------|-------|
| Bauxite | -0'94 | -0'51 | -0'26 | +2'2 | +8'8 | +18'0 |
| Halloysite | -8'5 | -3'6 | -2'6 | +0'38 | +9'5 | +34'3 |
| Kaolin | 0'0 | +4'2 | +4'2 | +4'5 | +7'0 | +18'0 |
| Limonite | -1'5 | -1'8 | -3'1 | -0'88 | +0'75 | +11'8 |
| Montmorillonite | -5'1 | -1'7 | -1'5 | +0'38 | +4'5 | +10'5 |

* Data taken from the paper of Raychaudhuri and Basuraychaudhuri (*loc. cit.*, p. 145.)

It will be observed from Fig. 6 that the uptake of base by pure gels of silica and alumina are comparatively small. The uptake of base is

M. equiv. of the base taken per 100 g. of sol (oven-dry basis).

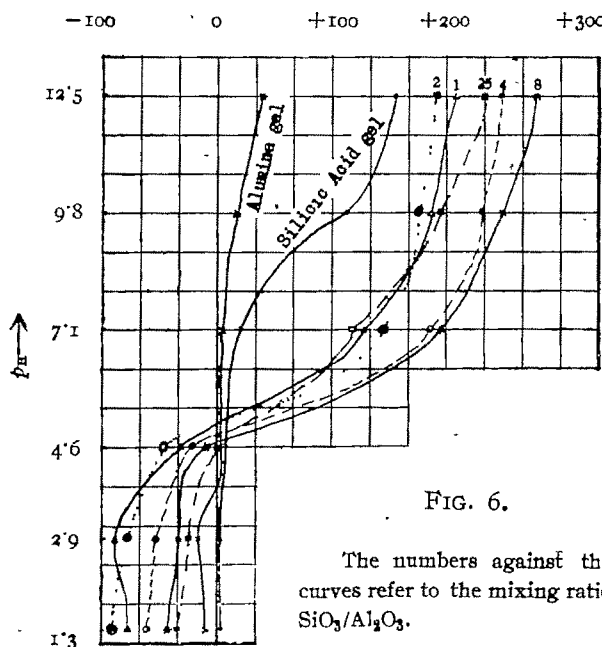
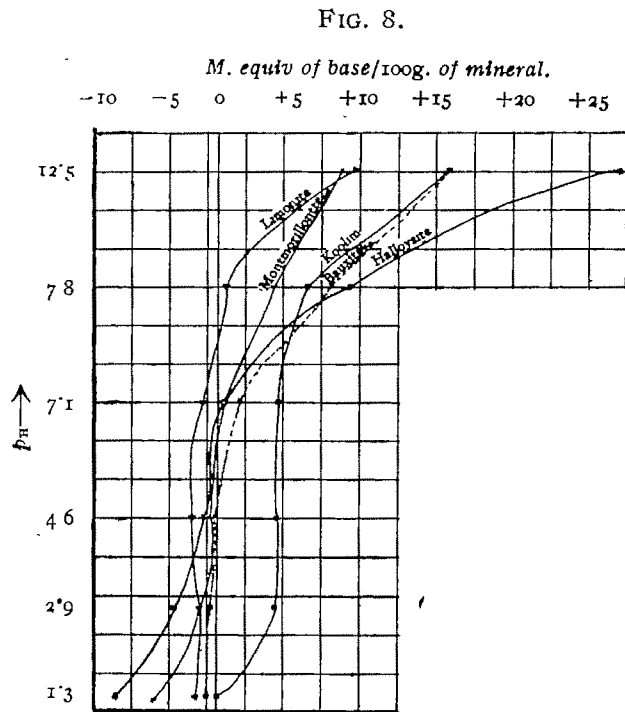
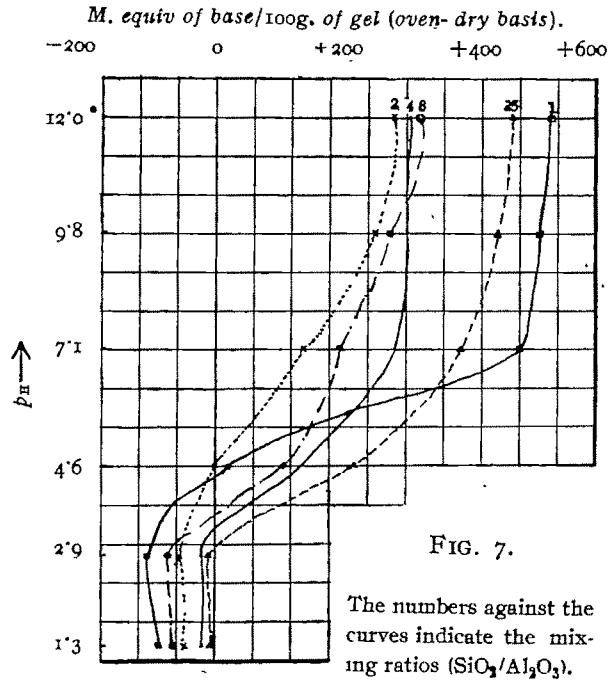


FIG. 6.

The numbers against the curves refer to the mixing ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$.

greatest with precipitated gel having $\text{SiO}_2/\text{Al}_2\text{O}_3=8$. This is in accordance with current view (*cf.* Weigner, *loc. cit.*) that at a particular $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio the base exchange capacity is a maximum. The conclusions from ion adsorption experiments (*vide* Fig. 2) also point to such a maximum. But the uptake of acid ($\text{HCl } 0.04N$, *vide* Tables XXI and XXII) does not give a maximum with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ values. This is due to the acidic nature of SiO_2 . Also the base combining capacity of sample with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio=1 is higher than with a sample with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio=2. This may be explained by the fact that a large amount of aluminium facilitates both acid and base uptake due to the amphoteric nature of alumina. But pure alumina does not give high values, as the pure gel loses its structure. Fig. 7 shows that precipitates with silica-alumina ratios of 2 and 4 give buffer curve which are similar, only a shift to the acid side happens, corroborating the view postulated before that these two samples would, to some extent, show similar properties. As expected, precipitates with silica-alumina ratios of 8 and 25 give dissimilar curves. Precipitate with silica-alumina ratio of 1 gives a curve which has got the highest buffer capacity. All the curves in Fig. 7



have one characteristic *i.e.* at low p_H the acid uptake decreases with decrease of p_H . This may be due to the presence of aluminium ions on the surfaces of the precipitates, set free by treatment with hot $AlCl_3$ solution (*cf.* the buffer curve for Al_2O_3 gel in Fig. 8 at low p_H values). Fig. 8 shows that of all the clay-forming minerals studied, halloysite possesses maximum buffer capacity, next in order being montmorillonite and bauxite. Kaolin and limonite possess very low buffer capacity.

A comparison of Fig. 8 shows that the buffer curves of the naturally occurring minerals do not correspond much in nature to the buffer curves obtained with electro dialysed precipitated gels of aluminosilicates and of the same gels after treatment with hot 10% $AlCl_3$ solution and subsequent electro dialysis. Moreover, the buffer capacities of the naturally occurring minerals are much lower compared to those of the synthetic gels. This dissimilarity in the nature of the buffer curves of the synthetic and naturally occurring clay-forming aluminosilicates suggests that ageing of the precipitates may have considerably altered their properties. It would therefore be interesting to compare the properties of synthetic aluminosilicate gels after considerable ageing and of naturally occurring aluminosilicates which could not be undertaken in the present work.

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INFLUENCE OF TEMPERATURE ON THE SLOW AND INDUCED OXIDATION OF GLUCOSE IN THE DARK.

By N. R. DHAR.

Aqueous solutions of glucose containing sodium hydrogen phosphate have been oxidised in the dark at temperatures 10°, 20°, 30°, 40° and 50° by passing a current of air and the temperature coefficient of this reaction for a 10° rise between 10° and 30° is approximately 2.5 and between 30° and 50° it is less than unity. When the same reaction is carried on in presence of ferrous hydroxide as inductor, the temperature coefficient between 10° and 30° is approximately 1.8 and between 30° and 50° it is less than unity. When cerous hydroxide is used as an inductor the velocity of the reaction is greatly increased but the temperature coefficient is almost unity between 10° and 50°.

The slow and induced oxidation of glucose and other carbohydrates and of other energy-rich materials has been studied in these laboratories by several workers and the conclusions arrived at have been made use of in explaining the mechanism of oxidation in the animal body, plants and in soil. So far the experiments were carried on either in the diffused light or in bright light. But as the reactions in the animal body take place in the dark and under different temperatures, the study of these induced and slow reactions *in vitro* under these conditions may throw light on metabolic processes. The following experiments have been undertaken.

The reaction bottles employed were coated outside with Black Japan enamel to cut off light, carefully cleaned and dried and were fitted with rubber corks having double bores. Chemically pure glucose solutions together with inductors were put in these bottles and a current of air, freed from carbon dioxide by passing through a 50% solution of sodium hydroxide and tested by passing through baryta solution, was aspirated through the mixture in the reaction bottles which were maintained at various constant temperatures in thermostats.

The inductors used were freshly precipitated ferrous and cerous hydroxides and 20 c.c. of $N/10$ sodium hydrogen phosphate solution were also added to the glucose solution in the reaction bottle. The experiments were carried out at 10°, 20°, 30°, 40° and 50°.

After passing the total amount of air, the hydroxides were coagulated and precipitated by the addition of potassium sulphate. The mixture was filtered after warming it a little and the amount of unoxidised glucose was estimated by means of a standard Fehling's solution. Total volume of solution was 200 c.c. and the total amount of glucose in each case was equivalent to 0.2398 g. of CuO per 10 c.c. of glucose solution.

TABLE I.

| Temp. | CuO corresp. amount after oxidation without inductor (100 c.c. soln.) | % Oxidation of glucose without inductor. | CuO (100 c.c. solution) corresponding amount with 20 c.c. $\text{FeSO}_4 \equiv 0.5 \text{ g. Fe}_2\text{O}_3$. | % Oxidation of glucose in presence of Fe(OH)_2 as inductor. | CuO corresponding (100 c.c. soln) with 47.3 c.c. cerous chloride $\equiv 0.1 \text{ g. cerous hydroxide}$. | % Oxidation of glucose with cerous hydroxide as inductor. |
|-------|---|--|--|--|---|---|
| 10° | 0.2352 g. | 1.84 | 0.2344 g. | 3.10 | 0.1567 g. | 34.60 |
| 20° | 0.2286 | 4.51 | 0.2261 | 5.60 | 0.1557 | 34.96 |
| 30° | 0.2134 | 10.94 | 0.2158 | 9.95 | 0.1465 | 38.75 |
| 40° | 0.2252 | 6.01 | 0.2242 | 6.26 | 0.1450 | 43.70 |
| 50° | 0.2296 | 4.01 | 0.2270 | 5.10 | 0.1220 | 49.00 |

TABLE II.

| Temp. range ratio of vel. coeff. | Temp. coeff. without inductor. | Temperature coefficient with inductor. | |
|----------------------------------|--------------------------------|--|-------------------|
| | | Ferrous hydroxide. | Cerous hydroxide. |
| K_{20}/K_{10} | 2.45 | 1.8 | 1.01 |
| K_{30}/K_{20} | 2.42 | 1.77 | 1.11 |
| K_{40}/K_{30} | Less than unity | Less than unity | 1.12 |
| K_{50}/K_{40} | " | " | 1.11 |

It appears from Tables I and II that the velocity of the oxidation of glucose goes on increasing up to a certain optimum temperature, which, in the case of ferrous hydroxide or in its absence, lies between 30° and 40°. In the presence of cerous hydroxide as inductor, however, the velocity of oxidation goes on increasing continuously and the velocity is higher at 50° than at lower temperature. The anomalous behaviour of cerium is interesting. As the body reactions take place at an optimum temperature, the above observations on the oxidation of glucose without any inductor and in presence of inductors *in vitro* may be utilised in explaining the probable metabolism of glucose in the animal body.

A NOTE ON THE ACTION OF THIONYL CHLORIDE ON 2:3-OXYNAPHTHOIC ACID.

BY J. W. AIRAN AND S. V. SHAH.

Meyers (*Monatsh*, 1905, **22**, 791) on treating 2:3-oxynaphthoic acid with thionyl chloride at 50° obtained its acid chloride, m.p. 91-92°, whereas Kostanecki (*Ber.*, 1882, **25**, 1642) distilled 2:3-oxynaphthoic acid with acetic anhydride and obtained γ -dinaphthoxanthone.



(I)

The dehydration product obtained in the present investigation has been assigned a structure (I) on the strength of molecular weight determination. On being boiled with sodium hydroxide solution, the ring is opened up and 2:3-oxynaphthoic acid is re-obtained.

Attempts have been made to obtain Kostanecki's compound for comparison purposes, but only acetyl derivative is obtained. Kostanecki's compound is described as dissolving in concentrated sulphuric acid forming brown solution with fluorescence, but the dehydration product, obtained in the present investigation, does not behave similarly.

Thus thionyl chloride is not found to introduce sulphur atom in this case, as it does in the case of 1:2-oxynaphthoic acid (Airan and Shah, *J. Bombay Univ.*, 1942, **10**, 128) nor does it bring about either chlorination or acid-chloride formation, under the conditions described.

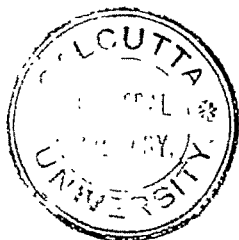
Thionyl chloride (30 c.c.) was added, 5 c.c. at a time, in about 20 minutes to 2:3-oxynaphthoic acid (5 g.) heated in an oil-bath at 110° in a distilling flask provided with a dropping funnel. The dry residue was extracted with chloroform, and ether was added to the chloroform solution when immediately a yellow solid separated. This was filtered, washed with ether, and treated with carbon tetrachloride in a Soxhlet apparatus to rid the compound of any free sulphur sticking to it, m.p. 240°, yield 50%. It gave no test for sulphur, hydroxyl group or carboxyl group. It is insoluble in dilute sodium hydroxide,

and has to be boiled with it in an evaporating dish for a fairly long time to dissolve it. From this solution a solid was obtained (by reprecipitation with hydrochloric acid), m.p. 214° (mixed m.p. with 2:3-oxynaphthoic acid). [Found: M. W. (freezing point in nitrobenzene), $155\frac{1}{3}$; Equiv., 189.2. $C_{11}H_6O_2$ requires M. W., 170; Equiv., 170].

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NITRATION OF 5-HYDROXY-4-METHYLCOUMARIN AND 5-HYDROXY-4-METHYLCOUMARIN-6-CARBOXYLIC ACID AND ITS METHYL ESTER.

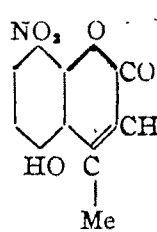
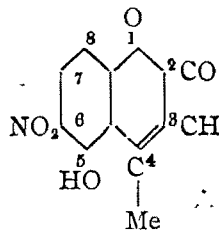
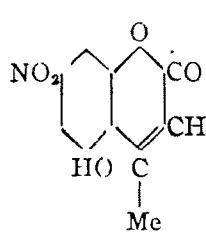
BY N. B. PAREKH AND R. C. SHAH.

5-Hydroxy-4-methylcoumarin on nitration at 0° affords 5-hydroxy-4-methyl-8-nitrocoumarin and at higher temperatures the 6,8-dinitro derivative. The nitration of 5-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester affords 8-nitro derivatives, and the 8-nitro-acid on decarboxylation gives 5-hydroxy-4-methyl-8-nitrocoumarin, identical with the mono-nitro product of 4-methyl-5-hydroxycoumarin.

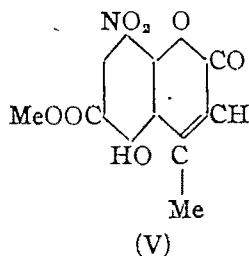
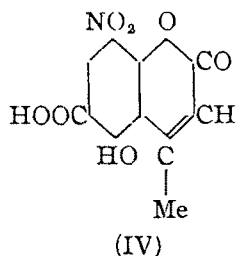
The nitration of coumarin itself and its hydroxy and methoxy derivatives has been investigated by a number of workers (Bleibtren, *Annalen*, 1855, **98**, 252; Tage, *Ber.*, 1887, **20**, 2110; Morgan, *J. Chem. Soc.*, 1904, **88**, 1233; Francis, *Ber.*, 1906, **39**, 3803; Clayton, *J. Chem. Soc.*, 1910, **97**, 1397; Pechmann and Cohen, *Ber.*, 1884, **17**, 2136; Pechmann and Obermiller, *ibid.*, 1901, **34**, 666; Fries and Lindemann, *Annalen*, 1848, **67**, 404; Dey and Krishnamurthi, *J. Indian Chem. Soc.*, 1927, **4**, 197; Dey and Kutti, *Proc. Nat. Inst. Sci.*, 1940, **6**, 641). As 5-hydroxy-4-methylcoumarin and its derivatives have become recently available (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228), it has been thought interesting to study the substitution in such derivatives and to find out the reactivity of 5-hydroxycoumarin nucleus. In this communication, the nitration of 5-hydroxy-4-methylcoumarin and 5-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester has been investigated.

5-Hydroxy-4-methylcoumarin (Sethna, Shah and Shah, *loc. cit.*) has been nitrated under different conditions. The mono-nitro product, (174-76°) is obtained without difficulty on treating the coumarin with a mixture of concentrated sulphuric acid and nitric acid (*d* 1.42) at 0°-5°.

The product (m.p. 174-76°) is boiled with concentrated ammonia; on acidification the unchanged product is recovered, showing that the nitro group does not enter the pyrone ring (*vide* Clayton, *loc. cit.*). Of the



following alternative structures, (I) is eliminated as OH is always *o-p*-directing. Of the remaining (II) and (III), 5-hydroxy-8-nitro-4-methylcoumarin structure (III) probably represents the product (m.p. 174-76°) as it gives only a feeble ferric chloride colouration since it corresponds to *p*-nitrophenol.



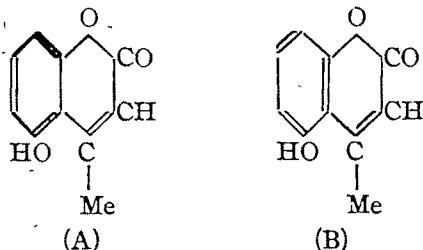
In order to establish the above structure definitely, the nitration of 5-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester has been studied. In this case, the position 6 is blocked up and the possibility for the entry of nitro group is only 8 or 3 position or both. Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate (Sethna *et al.*, *loc. cit.*), gives on nitration a mono-nitro product (m.p. 201-2°), which on hydrolysis gives the acid (m.p. 220-21°), identical in all respects to the nitro-acid obtained by the direct nitration of 5-hydroxy-4-methylcoumarin-6-carboxylic acid (Sethna *et al.*, *loc. cit.*) under the same conditions as in the case of the ester. The nitro-acid (m.p. 220-21°), is boiled with concentrated ammonia; but the original product is recovered on acidification, showing that NO₂ has not entered the pyrone ring. Thus the nitration has been effected in 8-position of the coumarin nucleus, in both the acid and the ester, yielding 5-hydroxy-4-methyl-8-nitrocoumarin-6-carboxylic acid (IV) and its ester (V) respectively.

The decarboxylation of the acid (IV) gives a product (m.p. 174-76°) identical in all respects with the nitration product of 5-hydroxy-4-methylcoumarin, which is thus definitely proved to be 5-hydroxy-8-nitro-4-methylcoumarin.

The nitration of 5-hydroxy-4-methylcoumarin at room temperature gives the dinitro product (m.p. 181-82°). Its behaviour with boiling ammonia shows that none of two NO₂ groups enters the pyrone ring. It has, therefore, been assigned the structure 5-hydroxy-4-methyl-6:8-dinitrocoumarin.

Pechmann and Obermiller (*loc. cit.*) found that in nitration of the 7-hydroxycoumarin, the nitro group had entered the position 8. The same coumarin shows reactivity in 8-position in other reactions also (*vide* Rangaswami and Seshadri, *Proc. Indian Acad. Sci.*, 1937, **6A**, 122; Späth and Pailer, *Ber.*, 1935, **68**, 941; Baker and Lothian, *J. Chem. Soc.*, 1935, 628; 1936, 275). The results of nitration of 5-hydroxy-4-methylcoumarin show the

reactivity in 8-position which is *para* to OH in 5-position of the coumarin nucleus. If the fixation of double bonds had taken place under the experimental conditions, the product should have been 6-nitro derivative. In this connection, it may be mentioned that 5-acyloxy-4-methylcoumarins undergo the Fries migration to give 6-acyl derivatives (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228, 1424; 1939, 1250). The results of the



present investigation show that 5-hydroxy-4-methylcoumarin reacts sometimes in form (A) and sometimes in form (B). Further work to elucidate this point more fully is being undertaken.

EXPERIMENTAL.

5-Hydroxy-8-nitro-4-methylcoumarin (III).—5-Hydroxy-4-methylcoumarin (0.5 g.), prepared according to the method of Sethna, Shah and Shah (*loc. cit.*), was added to a mixture of nitric acid (*d* 1.42, 0.8 c.c.) and concentrated sulphuric acid (1 c.c.), the temperature being kept within 0°-5° by keeping it in ice-bath. The reaction mixture was kept at the same temperature for 1 hour with stirring and the pasty mass then added to water. The product that separated was washed with water and sodium bicarbonate (5%, 5 c.c.), dried and crystallised from acetic acid (charcoal) in golden yellow prisms, m.p. 174-76° (efferv.), yield 0.2 g. It gives slight reddish colour with alcoholic ferric chloride. (Found: N, 6.7. $C_{10}H_7O_3N$ requires N, 6.33 per cent).

The nitro compound was boiled with concentrated ammonia but it was recovered unchanged.

Methyl 5-Hydroxy-8-nitro-4-methylcoumarin-6-carboxylate (V).—Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate (4 g.), prepared according to Sethna *et al.* (*loc. cit.*), was dissolved in glacial acetic acid (80 c.c.) and nitric acid (*d* 1.42, 32 c.c.) added drop by drop. It was then refluxed on a water-bath for 20-30 minutes, cooled and crystallised from acetic acid as golden yellow needles, m.p. 201-02°, yield 2 g. A further quantity was recovered from mother-liquor by extracting with ether. (Found: N, 5.13. $C_{12}H_9O_7N$ requires N, 5.0 per cent).

5-Hydroxy-8-nitro-4-methylcoumarin-6-carboxylic Acid (IV).—(i). The above ester (0.5 g.) was shaken up with sodium hydroxide (10%, 20 c.c.)

and kept for 60 hours. The solution was filtered and acidified. The solid crystallised from hot water as yellow needles, m.p. $220-21^{\circ}$ (efferv.), yield 0.2 g. (Found: N, 5.6. $C_{11}H_7O_7N$ requires N, 5.3 per cent).

(ii) The ester was conveniently hydrolysed by heating the above quantities of the ester and alkali on a water-bath for 20-30 minutes. This method is more convenient for hydrolysis of the ester than (i).

(iii) 5-Hydroxy-4-methylcoumarin-6-carboxylic acid (5 g.) was dissolved in hot glacial acetic acid solution and nitric acid ($d 1.42$, 40 c.c.) added to it while hot, and then the mixture refluxed on a water-bath for 20-30 minutes. It was cooled, diluted with ice-water, the product was collected, washed and crystallised from water as yellow needles, m.p. $220-21^{\circ}$ (efferv.), identical in all respects with 5-hydroxy-8-nitro-4-methylcoumarin-6-carboxylic acid obtained above, yield 2.4 g. The mixed m.p. was unaffected.

The acid gives effervescence with sodium and potassium bicarbonates forming sparingly soluble salts; it dissolves in alkali with non-fluorescent yellow colour, and gives red colour with alcoholic ferric chloride.

Decarboxylation of 5-Hydroxy-8-nitro-4-methylcoumarin-6-carboxylic Acid.—The acid (0.8 g.) was heated with water (20 c.c.), glacial acetic acid (8 c.c.) and concentrated hydrochloric acid (4 c.c.) in a sealed tube for 7-8 hours at $135^{\circ}-140^{\circ}$. The solution was filtered and extracted with ether. The acetic acid was removed over sodium hydroxide in a vacuum desiccator; the residue crystallised from glacial acetic acid (charcoal) as yellow prisms, m.p. $174-76^{\circ}$ (decomp.), yield 0.2 g. The product was identical in all respects with the nitration product of 5-hydroxy-4-methylcoumarin described before (mixed m.p.).

5-Hydroxy-6:8-dinitro-4-methylcoumarin.—5-Hydroxy-4-methylcoumarin (1 g.) in acetic acid solution (15 c.c.) was treated with concentrated nitric acid (8 c.c.) dropwise with shaking and cooling under tap. The mixture was left overnight, diluted with water; the product collected and crystallised from aqueous methyl alcohol as yellow prisms, m.p. $181-82^{\circ}$, yield 0.4 g. (Found: N, 10.8. $C_{10}H_6O_7N_2$ requires N, 10.5 per cent).

The dinitrocoumarin (0.2 g.) was dissolved in concentrated ammonia (10 c.c.) and boiled for nearly 3 hours. On acidification, the unchanged product, m.p. $180-82^{\circ}$, was recovered.

One of the authors (N. B. P.) thanks Dr. S. M. Sethna for his help and interest.

ALUMINIUM CHLORIDE—A NEW REAGENT FOR THE CONDENSATION OF β -KETONIC ESTERS WITH PHENOLS.
PART VII. THE CONDENSATION OF 4-NITRO-RESORCINOL WITH ETHYL ACETOACETATE.

BY N. B. PARKKH AND R. C. SHAH.

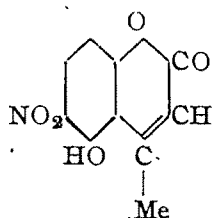
In continuation of the previous work, 4-nitroresorcinol has been successfully condensed with ethyl acetoacetate in the presence of aluminium chloride. The product has been proved to be 4-methyl-5-hydroxy-6-nitrocoumarin, which has been degraded to the corresponding mono- and dimethoxycinnamic acids. The formation of the 5-hydroxycoumarin derivative shows for the first time that under the experimental conditions, the chelation between the OH and NO₂ groups in 4-nitroresorcinol, leads to a fixation of the double bonds and consequent stabilisation of one of the Kekule forms.

In the previous parts of this series, it is shown that methyl β -resorcyate, β -resorcylic acid, resacetophenone and similar phenolic compounds condense with ethyl acetoacetate in the presence of aluminium chloride with the formation of otherwise difficultly accessible 5-hydroxycoumarins in good yields (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228; Sethna and Shah, *ibid.*, 1938, 1066; Shah and Shah, *ibid.*, 1938, 1424; Deliwala and Shah, *ibid.*, 1939, 1250; *Proc. Indian Acad. Sci.*, 1941, **13 A**, 352). The reactivity in 2-position of the resorcinol nucleus in the formation of the above 5-hydroxycoumarin derivatives is explicable on the view of fixation of double bonds in the benzene nucleus, the chelation between OH and COOR (R=H or Me) or CO'R (R=Me, Et, Ph, etc.) bringing about that state in presence of aluminium chloride (Shah and Shah, *loc. cit.*).

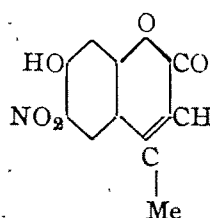
The condensation of 4-nitroresorcinol with ethyl acetoacetate described here has been undertaken to extend the above observations in the case of nitro group.

4-Nitroresorcinol on condensation with ethyl acetoacetate in the presence of aluminium chloride gives a product (m.p. 209-10°) in poor yield. The structure, 5-hydroxy-6-nitro-4-methylcoumarin (I) has been assigned to it on the following grounds: (i) It gives a strong ferric chloride colouration and dissolves in alkali with non-fluorescent yellow colour; (ii) it is found non-identical by direct comparison with 5-hydroxy-8-nitro-4-methylcoumarin obtained by decarboxylation of 5-hydroxy-8-nitro-4-methylcoumarin-6-carboxylic acid (*This issue*, p. 340); (iii) its non-identity with 7-hydroxy-6-nitro-4-methylcoumarin (II) (Chakravarti and Banerjee, *J. Indian*

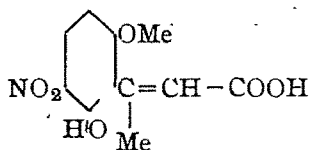
Chem. Soc., 1937, **14**, 37) as shown by direct comparison ; and (iv) the condensation product has been definitely proved to be a coumarin derivative by converting it into methylated cinnamic acids (III) and (IV) by the modified method of Shah and Shah (*J. Univ. Bombay*, 1938, **7**, 213).



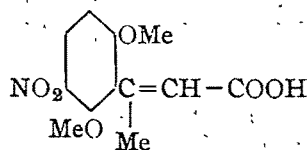
(I)



(II)

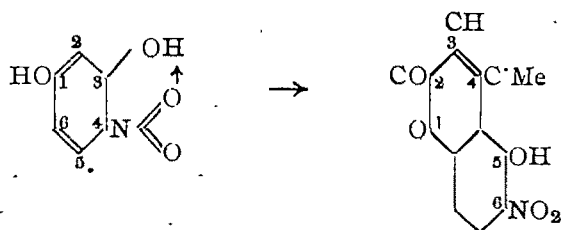


(III)



(IV)

It is generally accepted that the chelation between OH and COMe in resacetophenone and OH and COOMe in methyl β -resorcyate stabilises one of the Kekule forms (Baker and co workers, *J. Chem. Soc.*, 1934, 1686 ; 1935, 628, *et seq.*) but in case of 4-nitroresorcinol no definite conclusion seems to have been arrived at on this point (Baker and Lothian, *J. Chem. Soc.*, 1936, 276). The formation of 5-hydroxy-6-nitro-4-methylcoumarin in the present condensation shows that chelation between NO₂ and OH in 4-nitroresorcinol under the experimental conditions, leads to a fixation of the double bonds in the benzene nucleus, as shown below, one of the Kekule forms being thus stabilised, and the carbon atom, which is joined to the carbon atom bearing the hydroxyl group by a double bond, being activated.



E X P E R I M E N T A L.

Condensation of 4-Nitroresorcinol with Ethyl Acetoacetate in presence of Aluminium Chloride: Formation of 5-Hydroxy-6-nitro-4-methylcoumarin (I).—Anhydrous 4-nitroresorcinol (4 g., 1 mol.), and acetoacetic ester (5.2 g., 1.1 mol.) were dissolved in dry nitrobenzene (15 c.c.). Aluminium chloride (E. P. 10.2 g., 3 mols.) in dry nitrobenzene (25 c.c.) was added and the mixture protected from moisture was heated at 110–15° for 1 hour. The mixture was cooled, crushed ice and concentrated hydrochloric acid (5 c.c.) added and nitrobenzene steam-distilled. After removal of nitrobenzene, it was filtered while hot to remove some tarry material and kept in frigidaire. Next day the substance separated in fine needles along with some uncondensed product. The mixture was dissolved in excess of hot water (100 c.c.) and kept in frigidaire for 4–5 hours, when 5-hydroxy-6-nitro-4-methylcoumarin separated in fine lustruous needles; recrystallised from hot water and a drop of concentrated hydrochloric acid, it had m.p. 209–10°, yield 0.2 g. (Found: C, 54.2; H, 3.3; N, 6.2. $C_{10}H_7O_5N$ requires C, 54.3; H, 3.2; N, 6.3 per cent).

It is sparingly soluble in alcohols, benzene, chloroform and 10% sodium hydroxide; it is more soluble in acetone and acetic acid. It gives with alkalis a deep yellow non-fluorescent colour characteristic of a 5-hydroxycoumarin (Collie and Chrystall, *J. Chem. Soc.*, 1907, **91**, 1804; Dey, *ibid.*, 1915, **107**, 1614) and intense violet colouration with alcoholic ferric chloride.

The above condensation was attempted using dry ether as a solvent but no definite product could be isolated. It may be noted here that the quality of aluminium chloride affects considerably the quality and yield of the condensation product, and that the condensation in small lots (3 to 4 g.) gives correspondingly increased yields than by working with large quantities of 4-nitroresorcinol at a time.

The *methyl ester*, prepared by methyl iodide in presence of acetone and potassium carbonate, crystallised from hot water as clusters of tiny needles, m.p. 132–33°. (Found: C, 56.2; H, 3.6; N, 6.2. $C_{11}H_9O_5N$ requires C, 56.2; H, 3.8; N, 6.0 per cent).

Conversion of 5-Hydroxy-6-nitro-4-methylcoumarin into o-Methoxycinnamic Acids: Formation of 6-Hydroxy-2-methoxy- and 2:6-Dimethoxy-5-nitro- β -methylcinnamic Acids (III and IV).—To the coumarin (0.2 g.) in acetone solution was added dimethyl sulphate (2 c.c.) and the solution treated with sodium hydroxide (10%, 10 c.c.) with continuous shaking and cooling under tap water. More alkali and dimethyl sulphate (2 c.c.) were added with shaking and the mixture distinctly alkaline left overnight. It was filtered, acidified with dilute hydrochloric acid and extracted with ether,

The acid crystallised from hot water and a drop of concentrated hydrochloric acid, m.p. $162-63^{\circ}$ (efferv.). It gives violet colouration with alcoholic ferric chloride and dissolves in sodium bicarbonate solution with effervescence. (Found : C, 50.8 ; H, 4.9. $C_{11}H_{11}O_6N$, $\frac{1}{2}H_2O$ requires C, 50.4 ; H, 5.0 per cent).

If the above conversion is carried out at the temperature of water-bath using more dimethyl sulphate (7 c.c.) and stronger alkali (20%), 2 : 6-dimethoxy - 5 - nitro - β - methylcinnamic acid is obtained, which crystallises from hot water, m.p. $206-8^{\circ}$. It decolourises bromine water and potassium permanganate solution and gives no ferric chloride colour test. (Found : C, 53.6 ; H, 5.1 ; N, 4.9. $C_{12}H_{13}O_6N$ requires C, 53.9 ; H, 4.9 ; N, 5.2 per cent).

All analyses are micro-determinations by Mr. M. R. Patkar, M.Sc. of this Institute.

One of the authors (N. B. P.) thanks Dr. S. M. Sethna, M.Sc., Ph.D. for his interest and help.

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PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N.C.S.- PART XII. PHENYL- CYANAMIDE, ITS PROPERTIES AND DERIVATIVES. THE PHENYLHYDRAZINE α -CARBOXYLIC ACID.

BY RAMCHANDRA SAHASRABUDHEY AND HANS KRAHL.

Phenylcyanamide has been obtained by the desulphurisation of phenylthiocarbamide by copper acetate in alkaline or neutral medium. The properties of phenylcyanamide and of its derivatives have been investigated and the isolation of the hydrochloride of phenylhydrazine- α -carboxylic acid is described.

The close relationship of phenylcyanamide with phenylthiocarbamide necessitated an investigation of its properties because it appears not to have been systematically studied and the data are incomplete and misleading. The easiest method of its preparation is by desulphurisation of phenylthiocarbamide in an alkaline medium. Lead acetate, lead oxide and benzyl chloride were used for this purpose by the earlier workers (Rathke, *Ber.*, 1879, **12**, 772; Feuerlein, *ibid.*, p. 1602; Hofmann, *Ber.*, 1885, **18**, 3217; Berger, *Monatsh.*, 1884, **5**, 317; Traube and Wedelstadt, *Ber.*, 1900, **33**, 1383; Fromm, *Ber.*, 1895, **28**, 1302). We have found copper acetate to act in an analogous manner. In $N/2$ alkaline medium the yields are 75 and 65% respectively for lead and copper acetate. An excess of copper acetate or lead acetate does not affect the yield but an increase in the alkalinity of the medium from $N/2$ to $2N$ concentration increases the yield by about 10%. The action of copper acetate is remarkable in that it can also desulphurise phenylthiocarbamide in an aqueous medium; the yield of phenylcyanamide is, however, poor.

Hofmann and Feuerlein (*loc. cit.*) assigned the compositions $\text{Ph} \cdot \text{NH} \cdot \text{CN}, \frac{1}{2} \text{H}_2\text{O}$ and $(\text{NH} : \text{C} : \text{NPh})_2 \cdot 3\text{H}_2\text{O}$ respectively to the hydrates of the compound. Our results, however, show that the compound is a cyanamide and not carbodiimide and that different hydrates are formed at different temperatures.

The hydrates of phenylcyanamide. At about 30° monohydrate is chiefly formed while at 0° to 15° trihydrate with possibly smaller quantities of a still higher hydrate is the chief product. These various hydrates lose water of crystallisation spontaneously at ordinary temperatures or on warming and it is probably due to this property that Hofmann and Feuerlein assigned the above formulae. When dehydrated in a vacuum desiccator over

concentrated sulphuric acid or otherwise (*vide infra*) they are converted into anhydrous phenylcyanamide, which is a thick viscous liquid.

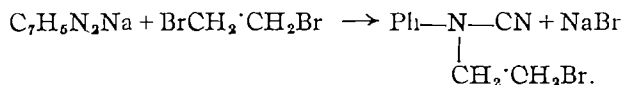
Polymerisation. Phenylcyanamide in absence of a solvent undergoes quick polymerisation, triphenylisomelamine (Hofmann, *loc. cit.*) being exclusively formed. The crystals of the hydrate are completely changed when heated on a water-bath for half an hour. At ordinary temperatures the hydrate takes about one week, whilst the anhydrous product completely polymerises within 48 hours. The kinetics of polymerisation could not be studied owing to difficulties in the estimation of the compound in aqueous solutions.

Phenylcyanamide is very soluble in ether and an ethereal solution, dehydrated over sodium sulphate, keeps unchanged for long periods. In acetone also it is easily soluble and this solution has good keeping qualities but a benzene solution throws down the insoluble triphenylisomelamine in a comparatively short time.

Estimation. Conditions for the estimation of phenylcyanamide in aqueous solution have been ascertained. It is precipitated as silver salt with an excess of silver nitrate, the excess being then volumetrically estimated.

Reduction of phenylcyanamide Phenylcyanamide is reluctant to undergo reduction. Ammonia and aniline were detected when reduced with zinc and sodium hydroxide. It may be recalled that all attempts to reduce phenylthiocarbamide without breaking it down have failed.

Action of metallic sodium on anhydrous phenylcyanamide. A sodium derivative with the composition $C_7H_5N_2Na$ is obtained. When heated it melts above 300° and then burns off leaving a residue of sodium cyanide. The structure of the sodium salt is PhN^+NaCN as suggested by the following reaction



Calcium chloride in ethereal solution probably throws down the calcium salt but this has not been examined. Discussion of the bearing of these results on the problem of constitution of phenylthiocarbamide is postponed pending the completion of further investigations, now in progress.

EXPERIMENTAL.

Preparation of Phenylcyanamide.—Phenylthiocarbamide (5 g.) was dissolved in about 100 c.c. of boiling water and to this were added the requisite quantities of alkali and the lead or copper acetates, also in boiling hot solution. The quantity of alkali was so taken as to completely cover the

neutralisation of the acetic acid of the salt added with enough excess to render the medium alkaline to the desired concentration. The total bulk of the mixture varied between 130 and 150 c.c. Immediately on addition of the lead or copper salt a black precipitate came down. The mixture was boiled for 10 minutes, then cooled and filtered. The filtrate was surrounded with ice and phenylcyanamide precipitated with a slight excess of strong acetic acid.

Determination of the Water of Hydration.

(i) Phenylcyanamide was dissolved in hot water and the crystals that came down at about 30° collected and dried. Known weights of these were allowed to polymerise at ordinary temperatures as also by heating on a water-bath till the m.p. and weight were constant. Water of hydration is lost in this process. In various experiments 17.5 to 22.0 g. of water were found to have combined with every 118 g. of $\text{PhNH}\cdot\text{CN}$ indicating that at about 30° monohydrate is chiefly obtained.

(ii) In another set of experiments anhydrous phenylcyanamide was rehydrated with ice-cold water. These samples when dehydrated were found to contain about 3 moles of water for every mole of $\text{PhNH}\cdot\text{CN}$. In one experiment as many as 4 moles of water were found.

(iii) Measurements of heats of hydration were conducted at 10°, 15° and 20° but almost constant values were obtained.

Polymerisation of Phenylcyanamide.

When anhydrous phenylcyanamide or the hydrate was allowed to stand at ordinary temperatures or warmed triphenylisomelamine, crystallisable from dilute alcohol, was obtained, m.p. 185°. (Found: N, 23.4. Calc. for triphenylisomelamine: N, 23.7 per cent).

A benzene solution also deposited triphenylisomelamine. Aqueous solution of phenylcyanamide also deposits the crystals of triphenylisomelamine.

Hydrolysis of Phenylcyanamide.

Action of Water and of Aqueous Acids and Alkalis.—Solubility of phenylcyanamide in water is less than 1%. In neutral solutions hydrolysis to phenylurea is not observed but polymerisation to triphenylisomelamine occurs followed by other complicated changes: First into a compound which crystallises from water in long white fibrous crystals, m.p. 209°. This change takes place even at ordinary temperatures and also in alcoholic solutions and is accelerated in a slightly alkaline medium. On prolonged

boiling with water or alkali it redissolves undergoing further chemical changes, probably forming some oxy derivative. Phenylcyanamide is easily soluble in glacial acetic acid and in aqueous solutions of mineral acids. In aqueous acidic solutions there is no evidence of polymerisation but it is quantitatively hydrolysed to phenylcarbamide. The rate of hydrolysis in mineral acid solutions has been found greater than in acetic acid solutions.

Aqueous caustic alkalis and ammonia simply dissolve phenylcyanamide. Evidently the alkaline metal salts are formed in solutions, and even in presence of an excess of alkali it does not undergo any further changes, but can be precipitated by acids in the form of its hydrates.

Solutions of phenylcyanamide in dilute aqueous acetic acid and mineral acids were allowed to stand at ordinary temperatures. Estimations of phenylcyanamide in these were done after every 24 hours. It was found that the strength of mineral acid solutions decreased faster than acetic acid solutions. On evaporating these solutions on a water-bath pure samples of phenylcarbamide were left behind. Triphenylisomelamine could not be detected.

Estimation of Phenylcyanamide.— $M/10$ solution of phenylcyanamide in $N/4$ sodium hydroxide solution was used. The solution was first rendered acidic with known quantities of glacial acetic acid and then silver salt of phenylcyanamide precipitated with an excess of standard silver nitrate solution.

The mixture was allowed to stand for 5 minutes, filtered and the filtrate with the washings estimated for silver nitrate using $N/20$ ammonium thiocyanate by Volhards' method. The effect of dilution was studied by adding distilled water to the phenylcyanamide solution before precipitation. Effect of addition of some mineral acid salts and large excess of silver nitrate was also studied. Phenylcyanamide in pure aqueous or alkaline solutions could be estimated with reasonable accuracy when the strength was below $M/30$ or $M/35$. In pure aqueous medium or in presence of excess of acetic acid (enough to render the solution N to $2N$) it could be precipitated as the silver salt with an excess of aqueous silver nitrate solution, the excess being estimated by Volhards' method. Excess of silver nitrate did not interfere nor did an excess of acetic acid up to a concentration of approximately $3N$. In higher concentrations of acetic acid or in more dilute solutions of phenylcyanamide the precipitation of silver salt was not complete and low values were obtained.

In solutions which did not contain alkali there was no need of addition of acetic acid, while if a large proportion of alkali be present, acetic acid had to be increased proportionately to suppress the hydroxyl ions. Presence of

mineral acids and their salts interfered. The chief limitation of this method, however, is the fact that the transformation products of phenylcyanamide also form insoluble silver salts.

Action of dry HCl gas on Anhydrous Phenylcyanamide.—Dry HCl gas gave a pale brown liquid from an ethereal solution of anhydrous phenylcyanamide. This when immediately treated with water reverted to phenylcyanamide, hydrochloric acid being dissolved away but if warmed on a water-bath for about half an hour it crystallised as white needles, m.p. 118° .

The crystals are hydrolysed to phenylcarbamide liberating free acid on treatment with water. The HCl and $\text{PhNH}\cdot\text{CN}$ are present in 1 : 1 ratio indicating that the crystalline derivative is $\text{PhNH}\cdot\text{CN}\cdot\text{HCl}$, M.W. 153.5.

Action of Concentrated Sulphuric Acid on Anhydrous Phenylcyanamide.—Concentrated sulphuric acid when gradually added to an ethereal anhydrous solution of phenylcyanamide heat was generated and a very viscous, pale brown, clear liquid separated out. This was thoroughly washed with ether and freed from impurity by warming on a water-bath. When treated with water, like the hydrochloride it was hydrolysed to phenylcarbamide and sulphuric acid, the quantities obtained indicating the composition, $\text{PhNH}\cdot\text{CN}\cdot\text{H}_2\text{SO}_4$. The liquid does not show any definite boiling point. When heated at 200° for 4 hours it is transformed into sulphanilic acid as shown by the molecular weight, sulphur content, the bromo derivative and other properties of the product.

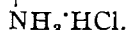
Action of Nitrous Acid on Phenylcyanamide.—To 50 c.c. of a 10% ethereal solution of phenylcyanamide were added 9 c.c. of concentrated hydrochloric acid. A concentrated aqueous solution of 4.5 g. of sodium nitrite was then gradually run in with constant stirring. When effervescence had ceased the deep yellow compound that had separated was collected, yield 5.5 g. The compound crystallises from 50% alcohol in peg-shaped slender crystals, m.p. $155-56^{\circ}$. [Found : N, 28.2. Calc. for $\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{CN}$: N, 28.5 per cent].

It contains a nitroso group as shown by its reaction with potassium iodide in presence of a mineral acid when iodine is liberated indicating the presence of free nitrous acid. It has, therefore, the composition $\text{PhN}(\text{NO})\text{CN}$. When digested on a water-bath for 3 to 4 hours with an excess of sodium hydroxide solution, ammonia was evolved and bright orange-red needles separated out on concentrating the liquors. This is probably the sodium salt of phenylnitrosocarbamic acid, $\text{PhN}(\text{NO})\cdot\text{COONa}$. It is very explosive. From an aqueous solution of this, silver nitrate precipitates a bright yellow silver salt which also when heated burns with a mild explosion. [Found :

Ag, 39.1; M. W., 277. Ph.N(NO)COOAg requires Ag, 39.5 per cent. M.W., 273].

Hydrochloric acid throws down a very pale yellow compound from the aqueous solutions of the sodium salt. This is probably the free acid. It does not show any definite melting point.

Reduction of the Phenylnitrosocarbamic Acid.—The sodium salt was warmed for a few minutes with an excess of tin and dilute hydrochloric acid, and the clear solution concentrated on a water-bath when a mixture of the crystals of SnCl_2 and the reduction product separated out. They were dissolved in water and tin removed as SnS by passing H_2S . When completely freed of tin salts the residue was crystallised from dilute hydrochloric acid (animal charcoal). This is, $\text{Ph}\cdot\text{N}\cdot\text{COOH}$, the hydrochloride of phenylhydrazine- α -carboxylic acid.



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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART XI. QUANTITATIVE POTENTIOMETRIC DETERMINATION OF AROMATIC AMINES.

BY BALWANT SINGH AND AHSANULHAQUE REHMANN.

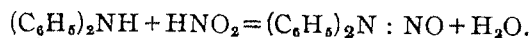
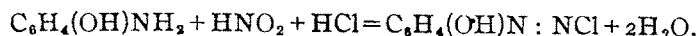
o-Nitroaniline, *p*-nitroaniline and 2:4-diaminophenol dihydrochloride have been estimated by titrating them potentiometrically against potassium iodate in presence of hydrochloric acid and *o*-phenylenediamine, *o*-aminophenol, *p*-aminophenol and diphenylamine against nitrous acid, using a platinum electrode coupled with a saturated calomel electrode at 15°.

The potentiometric method for the determination of the end-point in the titration of aromatic compounds with bromate in the presence of bromide has been applied by Callan and Horrobin (*J. Soc. Chem. Ind.*, 1929, **47**, 334). Singh and Singh (*J. Indian Chem. Soc.*, 1939, **16**, 346) used potassium chlorate and hydrochloric acid as a chlorinating agent in the potentiometric determination of aromatic compounds.

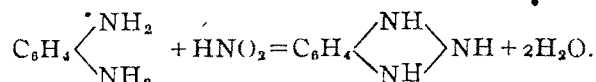
o-Nitroaniline, *p*-nitroaniline and 2:4-diaminophenol dihydrochloride can be chlorinated with potassium iodate in presence of hydrochloric acid and the reaction can be used for the potentiometric determination of these compounds.

When a solution of an aromatic amine is diazotised, free nitrous acid is formed at the completion of the reaction. A solution of nitrous acid in contact with a platinum electrode gives a definite potential. Muller and Dachzelt (*Z. Elektrochem.*, 1925, **31**, 662) studied the titration of aniline, xylydine and aminoazobenzene disulphonic acid. They found that the potential requires some time to become steady during the titration. Attempts were made to accelerate the reaction using higher temperatures. It was found that at 20° or below, the results were accurate. It is not necessary, therefore, to cool the mixture in ice during the titration. Singh and Ahmad (*J. Indian Chem. Soc.*, 1938, **15**, 416) applied the diazotisation method in the estimation of aromatic amines at 15°.

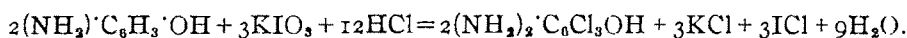
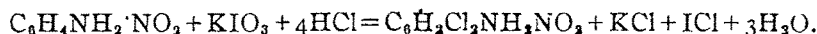
Sodium nitrite, in presence of an acid, reacts with *o*-aminophenol, *p*-aminophenol and diphenylamine. The reactions are represented by the following equations :



When a dilute solution of sodium nitrite is added to a dilute solution of *o*-phenylenediamine, azoaminobenzene is formed according to the equation (Ladenburg, *Ber.*, 1887, 9, 221) :



The following equations represent the reactions between potassium iodate and *o*-nitroaniline, *p*-nitroaniline and 2 : 4-diaminophenol in presence of hydrochloric acid.



These reactions have been made use of in the quantitative estimation of *o*-nitroaniline, *p*-nitroaniline and 2 : 4-diaminophenol dihydrochloride and *o*-aminophenol, *p*-aminophenol, *o*-phenylenediamine and diphenylamine by the potentiometric method.

EXPERIMENTAL.

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in a solution to be titrated, was coupled with a saturated calomel electrode through an agar agar-potassium chloride bridge. The cell was placed in a water-bath the temperature of which was maintained at 15°. E.M.F. of the cell was read on a potentiometer.

A known weight of the organic compound (*o*-nitroaniline, *p*-nitroaniline and 2 : 4-diaminophenol dihydrochloride) was mixed with water and a required amount of concentrated hydrochloric acid (Analar) was added to keep its concentration above 4*N*. The solution was titrated potentiometrically against standard potassium iodate solution. The mixture was kept stirred very thoroughly with a mechanical stirrer.

o-Phenylenediamine was titrated in presence of hydrochloric acid (Analar) and *o*-aminophenol, *p*-aminophenol and diphenylamine were titrated in presence of sulphuric acid (Analar), against standard sodium nitrite solution. On each addition of the titrant, the mixture was thoroughly stirred by means of a mechanical stirrer. The potentiometric readings were recorded 5 to 10 minutes after the addition of the reagent when the potential acquired a steady value.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of each set, is recorded in the following tables.

FIG. 1.

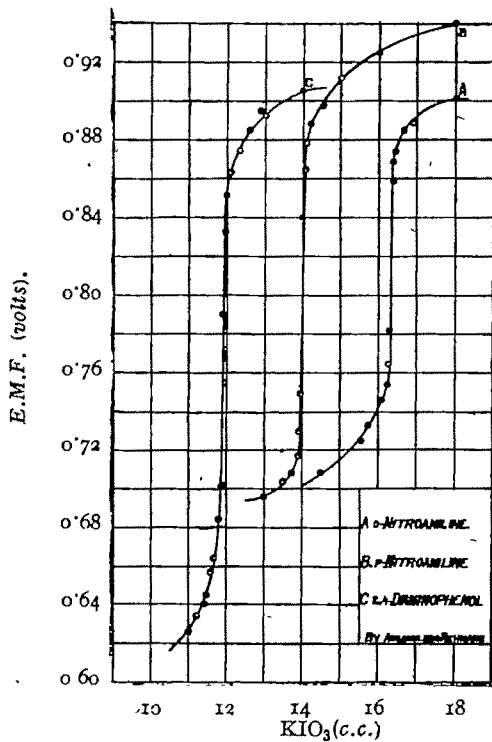


FIG. 2.

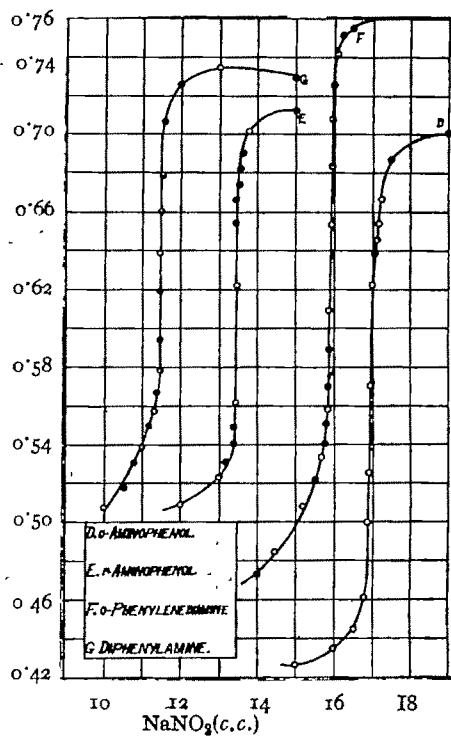


TABLE I.

0.0970 G. of *p*-nitroaniline mixed with 20 c.c. of water and 25 c.c. of concentrated hydrochloric acid and titrated against *M*/20-potassium iodate.

| KIO ₃ | E.M.F. | H/C. | KIO ₃ | E.M.F. | H/C. |
|------------------|------------|----------------|------------------|------------|----------------|
| | | (m. volt/c.c.) | | | (m. volt/c.c.) |
| 0.00 c.c. | 0.470 volt | | 13.90 c.c. | 0.727 volt | |
| 2.00 | 0.641 | 86 | 13.95 | 0.759 | 640 |
| 5.00 | 0.648 | 2 | 14.00 | 0.840 | 1620 |
| 7.00 | 0.654 | 3 | 14.05 | 0.864 | (max.) |
| 9.00 | 0.662 | 4 | 14.10 | 0.878 | 480 |
| 10.50 | 0.673 | 8 | 14.20 | 0.887 | 280 |
| 12.00 | 0.685 | 8 | 14.50 | 0.898 | 90 |
| 13.00 | 0.696 | 11 | 15.00 | 0.911 | 37 |
| 13.50 | 0.703 | 14 | 16.00 | 0.926 | 26 |
| 13.70 | 0.708 | 25 | 18.00 | 0.940 | 15 |
| 13.80 | 0.712 | 40 | 21.00 | 0.956 | 7 |
| 13.85 | 0.717 | 100 | 25.00 | 0.968 | 5 |
| | | 200 | 30.00 | 0.981 | 3 |

TABLE II.

0.1465 G. of *p*-aminophenol mixed with 30 c.c. of 30% sulphuric acid and titrated against *M*/10-sodium nitrite.

| NaNO ₂ | E.M.F. | E/C (m.volt/c.c.) | NaNO ₂ | E.M.F. | E/C (m.volt/c.c.) |
|-------------------|------------|----------------------|-------------------|------------|----------------------|
| 0.00 c.c. | 0.380 volt | | 13.375 c.c. | 0.552 volt | |
| 2.00 | 0.478 | 49 | 13.400 | 0.565 | 520 |
| 5.00 | 0.490 | 2 | 13.425 | 0.628 | 2520 (maximum) |
| 8.00 | 0.496 | 2 | 13.450 | 0.640 | 480 |
| 9.50 | 0.499 | 6 | 13.500 | 0.659 | 380 |
| 11.00 | 0.508 | 8 | 13.700 | 0.680 | 105 |
| 12.00 | 0.516 | 10 | 14.000 | 0.692 | 40 |
| 12.50 | 0.521 | 10 | 14.800 | 0.705 | 16 |
| 12.80 | 0.524 | 15 | 16.000 | 0.710 | 4 |
| 13.00 | 0.527 | 20 | 17.000 | 0.712 | 2 |
| 13.10 | 0.529 | 30 | 19.000 | 0.712 | — |
| 13.20 | 0.532 | 30 | 21.000 | 0.698 | — |
| 13.30 | 0.535 | 140 | 24.000 | 0.689 | — |
| 13.35 | 0.542 | 400 | 29.000 | 0.682 | — |

The titrations, one for each substance, are represented by the curves given in Fig. 1 and 2.

DISCUSSION.

In these titrations, it is evident that for the first set, with the addition of standard potassium iodate solution, the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise with further addition of the reagent.

In the second set, with the addition of standard sodium nitrite the E.M.F. rose steadily except in *o*-phenylenediamine, where it rose with the first addition of the reagent but with further addition the potential began to fall. This was followed by a steady rise till the equivalence point. At the equivalence point there was a sharp jump in potential in each case. After the equivalence point there was again a rise in the potential, followed by a steady fall.

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From the volume of the titrant required in each titration, corresponding to the equivalence point, the amount of the amine was calculated. The values obtained are compared in the following tables with the amounts of the amine taken.

TABLE III.

| <i>o</i> -Nitroaniline. | | <i>p</i> -Nitroaniline. | | 2 : 4-Diaminophenol dihydrochloride. | |
|-------------------------|-----------|-------------------------|-----------|--------------------------------------|-----------|
| Taken. | Found. | Taken | Found. | Taken. | Found. |
| 0.0917 g. | 0.0915 g. | 0.0970 g. | 0.0967 g. | 0.1001 g. | 0.1005 g. |
| 0.1133 | 0.1129 | 0.1408 | 0.1406 | 0.1562 | 0.1563 |
| 0.1958 | 0.1955 | 0.1891 | 0.1886 | 0.3127 | 0.3127 |
| 0.2918 | 0.2916 | 0.2816 | 0.2812 | 0.4731 | 0.4730 |
| 0.3855 | 0.3855 | 0.3918 | 0.3917 | 0.6276 | 0.6280 |

TABLE IV.

| <i>o</i> -Aminophenol. | | <i>p</i> -Aminophenol. | | Diphenylamine. | | <i>o</i> -Phenylenediamine. | |
|------------------------|-----------|------------------------|-----------|----------------|-----------|-----------------------------|-----------|
| Taken. | Found. | Taken. | Found. | Taken. | Found. | Taken. | Found. |
| 0.1294 g. | 0.1293 g. | 0.1465 g. | 0.1462 g. | 0.1943 g. | 0.1940 g. | 0.2216 g. | 0.2215 g. |
| 0.1858 | 0.1854 | 0.1973 | 0.1971 | 0.2933 | 0.2930 | 0.3513 | 0.3513 |
| 0.2333 | 0.2331 | 0.2932 | 0.2928 | 0.3928 | 0.3925 | 0.5039 | 0.5037 |
| 0.2827 | 0.2826 | 0.3920 | 0.3916 | 0.4942 | 0.4941 | 0.8599 | 0.8593 |
| 0.4198 | 0.4193 | 0.5397 | 0.5391 | 0.5840 | 0.5835 | 1.0002 | 1.0000 |
| 0.5854 | 0.5850 | | | 0.6929 | 0.6926 | | |

These results show that *o*-nitroaniline, *p*-nitroaniline, 2 : 4-diaminophenol dihydrochloride, and *p*-aminophenol, *o*-aminophenol, diphenylamine and *o*-phenylenediamine can be determined quantitatively by the potentiometric method.

The authors are indebted to the Khalsa College authorities for a research grant and for providing facilities for the work.

The author (A. Rehmann) is grateful to Major S. M. K. Mallick, Principal, Medical School, Amritsar, for his keen interest in the research work.

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CONDENSATION OF *o*-, *m*- AND *p*- THIOCRESOLS WITH *o*-BROMONITROBENZENE, 2:5-DICHLORONITRO- BENZENE AND 2:5-DIBROMONITROBENZENE.

BY PHULDEO SAHAY VARMA, K. S. VENKAT RAMAN AND N. H. MALANI.

Thiocresols (*o*-, *m*- and *p*-) have been condensed with *o*-bromonitrobenzene, 2:5-dichloronitrobenzene and 2:5-dibromonitrobenzene as a result of which 2'-nitro-2-methyldiphenyl sulphide, 2'-nitro-4-methyldiphenyl sulphide, 2'-nitro-4-methyldiphenyl sulphide, 4-chloro-2-nitro-4'-methyldiphenyl sulphide, 4-bromo-2-nitro-4'-methyldiphenyl sulphide and 4-chloro-2-nitro-2'-methyldiphenyl sulphide have been obtained

o-Nitrophenyl thioethers and their alkyl and halogen derivatives being required for another piece of research a reference to literature revealed that very few compounds of this series are known. Mauthner (*Ber.*, 1906, **39**, 3597) obtained 2-nitrodiphenyl sulphide by the condensation of sodium thiophenate and *o*-nitrobromobenzene in presence of copper powder; the same compound has been obtained by boiling sodium thiophenate and *o*-bromonitrobenzene in alcohol (Bourgeois and Uber, *Bull. Soc. chim.*, 1911, *iv*, **9**, 947) and by the action of thiophenol, potassium hydroxide and *o*-chloronitrobenzene in presence of copper-bronze (Roberts and Turner, *J. Chem. Soc.*, 1926, 1207). Mauthner also obtained *o*-nitrophenyl-*o*-tolyl sulphide from sodium *o*-thiocresolate and *o*-bromonitrobenzene. This compound is wrongly described as 4-nitro-*o*-phenyl-*o*-tolyl sulphide and 4-nitro-2-methyldiphenyl sulphide (Beilstein-Prager-Jacobson, "Organische Chemie," Vol. VI, p. 371). Loudon and Robson (*J. Chem. Soc.*, 1937, 242) have also obtained 4-chloro-2-nitro-4-methyldiphenyl sulphide by condensing 2:5-dichloronitrobenzene with *p*-thiocresol in alcohol.

In the experiments described in this paper the following condensation products have been obtained:—

2'-Nitro-2-methyldiphenyl sulphide, m p. 86°, b.p. 210-15°/18 mm.

2'-Nitro-3-methyldiphenyl sulphide, m p. 86-86.5°; b.p. 222°/18 mm.

2'-Nitro-4-methyldiphenyl sulphide, m p. 87.5°.

4-Chloro-2-nitro-4'-methyldiphenyl sulphide, m p. 121°.

4-Bromo-2-nitro-4'-methyldiphenyl sulphide, m p. 124°.

4-Chloro-2-nitro-2'-methyldiphenyl sulphide.

The products obtained with *m*-thiocresol are liquids and not in good quantities. It has not yet been possible to separate these products and obtain them in sufficient quantities for further investigation.

E X P E R I M E N T A L.

2'-Nitro-2-methyldiphenyl Sulphide.—*o*-Thiocresol (31 g.), *o*-bromonitrobenzene (51 g.) and copper-bronze (2 g.) were added to a warm solution of potassium hydroxide (10 g. in 10 c.c. water) and the solution refluxed on a sand-bath for 4½ hours at about 180°. It was then allowed to cool when the product solidified to a greenish black mass. The product was extracted successively for 4 times with carbon tetrachloride (50 c.c.; 30 c.c., 20 c.c., 10 c.c.) and the whole extract washed first with 15% potassium hydroxide solution to remove the unacted *o*-thiocresol and then with water, dried over fused calcium chloride and distilled under reduced pressure. The fraction distilling at 210-15°/16 mm. solidified to a yellow mass and gave needle-shaped yellow crystals (20 g.) on crystallisation from carbon tetrachloride, m.p. 86°. It is readily soluble in carbon tetrachloride, insoluble in petroleum ether, slightly soluble in alcohol and very easily in carbon disulphide and benzene. (Found: S, 12·8. $C_{13}H_{11}O_2NS$ requires S, 13·06 per cent).

2'-Nitro-3-methyldiphenyl Sulphide.—*o*-Bromonitrobenzene (12·5 g.), *m*-thiocresol (8 g.) and copper-bronze (0·3 g.) were added to a solution of sodium hydroxide (2·4 g.) in water (1·2 c.c.) and the solution refluxed for 4 hours at about 180° and the product treated as in the preceding case and distilled under reduced pressure. The fraction distilling at 222°/18 mm. solidified to a yellow solid mass. It was crystallised from carbon tetrachloride, m.p. 86·5°, yield 3·5 g. (Found S, 12·5. $C_{13}H_{11}O_2NS$ requires S, 13·06 per cent).

2'-Nitro-4-methyldiphenyl Sulphide.—*o*-Bromonitrobenzene (50 g.), *p*-thiocresol (31 g.), potassium hydroxide (14 g.) and copper-bronze (2 g.) were treated as above for 3½ hours on a sand-bath at about 200° and treated as in the preceding cases and the solid product boiled with animal charcoal and then crystallised from carbon tetrachloride when yellow prisms were obtained, m.p. 87·5°. (Found: S, 13·1. $C_{13}H_{11}O_2NS$ requires S, 13·06 per cent).

4-Chloro-2-nitro-4'-methyldiphenyl Sulphide.—*p*-Thiocresol (2 g.), 2,5-dichloronitrobenzene (2 g.), potassium hydroxide (0·6 g.) and water (1 c.c.) were refluxed on a sand-bath for 6 hours at about 180° and the product allowed to cool when a red solid mass was obtained. It was extracted thrice with carbon tetrachloride, washed with 15% potassium hydroxide solution and then with water, dried over fused calcium chloride and the solvent distilled off. The residue was crystallised from glacial acetic acid when orange prisms were obtained, m.p. 121°. It is easily soluble in warm carbon tetrachloride, soluble even in cold in benzene and carbon disulphide;

it is less soluble in petroleum ether, yield 1.7 g. (Found: S, 11.1. $C_{13}H_{10}O_2NCIS$ requires S, 11.4 per cent).

4-Bromo-2-nitro-4'-methyldiphenyl Sulphide.—2:5-Dichloronitrobenzene (2 g.) on similar treatment with *p*-thiocresol (3 g.) and potassium hydroxide (0.6 g.) in presence of copper-bronze gave orange-red crystals, m.p. 124°. It is very soluble in benzene and carbon disulphide, soluble on warming in carbon tetrachloride, much less soluble in petroleum ether, yield 1.8 g. (Found: Br, 24.4; S, 9.2. $C_{13}H_{10}O_2NBrS$ requires Br, 24.7; S, 9.8 per cent).

4-Chloro-2'-nitro-2-methyldiphenyl Sulphide.—*o*-Thiocresol (4 g.) and 2:5-dichloronitrobenzene (4 g.) and potassium hydroxide (1.2 g.) on similar treatment gave a distillate boiling at 200–205°/18 mm. which solidified slowly into bright yellow crystals, m.p. 82.5°. It is slightly soluble in rectified spirit and petroleum ether, more on warming. (Found: Cl, 12.3. $C_{13}H_{10}O_2NCIS$ requires Cl, 12.7 per cent).

4-Bromo-2-nitro-4'-methyldiphenyl Sulphone.—Potassium permanganate solution (0.7 g. in 100 c.c. of water) was added little by little to a solution of 4-bromo-2-nitro-4'-methyldiphenyl sulphide (1 g.) in glacial acetic acid and the excess of potassium permanganate was removed by passing sulphur dioxide and the whole allowed to stand overnight when a white precipitate was obtained. It was crystallised from carbon tetrachloride as beautiful needles, m.p. 132°. It turns pinkish on heating. (Found: S, 8.5. $C_{10}H_{10}O_4NBrS$ requires S, 8.9 per cent).

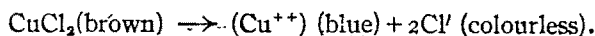
MAGNETIC STUDIES OF COLOUR CHANGES IN CUPRIC CHLORIDE

BY N. A. YAJNIK, RAM CHAND, A. N. KAPUR AND DIP CHAND JAIN.

Measurements of magnetic susceptibilities of cupric chloride, dissolved in various solvents, have been made under different conditions and the changes in magnetic susceptibility correlated with changes in colour of cupric chloride

It is well known that cupric chloride shows green colour in concentrated solutions, while it gives blue colour in dilute solutions. These changes of colour in cupric chloride solutions were first studied by Solly (*Phil. Mag.*, 1843, **iii**, 22, 367) and Gladstone (*J. Chem. Soc.*, 1856, 8, 212) who showed that a solution of cupric chloride in a small proportion of water is dark brown and the colour gradually passes through various shades of green, light green, bluish green, greenish blue and blue as the proportion of water is increased.

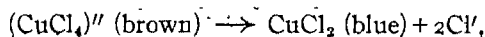
There are conflicting views regarding the mechanism of these colour changes. Ostwald ("Grundlinien der anorganischen Chemie", Leipzig, 1900) explained these colour changes by assuming that the undissociated molecules of cupric chloride are brown in colour and cupric ions (Cu^{++}) are blue in colour.



Thus there will be an equilibrium between undissociated molecules and ions depending upon the concentrations of the solution. Various shades of colour are produced as the degree of dissociation of cupric chloride goes on increasing with dilution. This assumption, however, could not be supported by the evidence obtained from spectroscopic investigation by Muller (*Ann. Physik*, 1903, **iv**, 12, 767) and Houston (*Proc. Roy. Soc. Edin.*, 1912, **32**, 40). Wiederman (*British Assoc. Rep.*, 1887, 364) attributed the colour changes to the progressive solvation of the solute. It was favoured by Chuard (*Archiv Sciences Geneve*, 1888, **iii**, 19, 477) and Rudorff (*Pogg. Ann.*, 1862, **116**, 64).



Donnan and Basset (*J. Chem. Soc.*, 1902, **81**, 939), however, attributed the colour changes on dilution to the formation and dissociation of complex ions.



The above hypothesis is supported by Watkins and Denham (*J. Chem. Soc.*, 1919, **115**, 1269) and Bhagwat (*J. Indian Chem. Soc.*, 1940, **17**, 52).

Getman (*J. Phys. Chem.*, 1922, **26**, 217) is in favour of a compromise between the hydration and complex-ion formation theories. He infers from the study of absorption spectrum of copper chloride that in dilute solutions halides form complexes with molecules of the solvent and in concentrated solutions complex ions are formed.

From the brief survey given above it will be evident that some work is required to decide between the conflicting views regarding the mechanism of colour changes. The magnetic susceptibility determinations have proved like the study of other physical properties useful in giving valuable information regarding the nature of salts in dissolved state. Thus it was felt that the study of magnetic susceptibilities of cupric chloride solutions under different conditions may throw some light on the subject.

Work has been done by Bhatnagar and co-workers (*J. Indian Chem. Soc.*, 1932, **9**, 341; 1936, **13**, 489) on colour changes of cobalt chloride in this laboratory and they have studied this problem by studying changes in the magnetic rotation and other susceptibility measurements.

EXPERIMENTAL.

The susceptibility measurements were made on a modified form of Guoy's balance. To maintain various temperatures, a silica tube wound round with a heating coil was used. In case of solute, susceptibilities have been calculated on the assumption that the magnetic susceptibility of the solution is equal to the sum of component susceptibilities.

$$\chi_s = \frac{\chi_{sol} - \chi_w(1 - C_s)}{C_s}$$

where χ_s , χ_w and χ_{sol} are magnetic susceptibilities of the solute, solvent and solution, and C_s is the amount of solute in one gram of the solution.

Magnetic susceptibility of conductivity water used in the present work was -0.720×10^{-6} . Cupric chloride (Merck's guaranteed reagent) was dehydrated according to the method of Sabatier (*Bull. Soc. chim.*, 1889, **iii**, **1**, 88).

Water, *n*-butyl, *n*-propyl, ethyl and methyl alcohols were the solvents used in the present investigation. These solvents were purified according to the methods given in the literature and their various constants are as shown in Table I.

TABLE I.

| Solvent. | Magnetic susceptibility. | Density. | Refractive index | Boiling point. |
|------------------|--------------------------|----------|------------------|----------------|
| Methyl alcohol | -0.665×10^{-6} | 0.7908 | 1.3275 | 64.5° |
| Ethyl alcohol | -0.744 | 0.7898 | 1.3610 | 78.0 |
| n-Propyl alcohol | -0.766 | 0.8035 | 1.3788 | 97.0 |
| n-Butyl alcohol | -0.7587 | 0.8140 | 1.3952 | 118.0 |

These constants are quite in agreement with constants given in the literature. $\chi(\text{CuCl}_2 \text{ anhydrous})$ at 35° was found to be 8.713×10^{-6} , and this CuCl_2 anhydrous was used in this work.

The amount of CuCl_2 present in different solutions was estimated iodometrically. The magnetic susceptibilities of CuCl_2 solutions of different concentrations in various solvents were studied in a Gouy type balance and the results are given in the following tables. All measurements were carried out at 35°.

TABLE II.

Variation in magnetic susceptibility of CuCl_2 dissolved in water.

| Comp. of CuCl_2 solution. | Magnetic susceptibility. Calc. | Obs. | χ (CuCl_2 solid). Calc. | Colour. |
|------------------------------------|-----------------------------------|------------------------|---|---------|
| 34.13% | 2.501×10^{-6} | 3.343×10^{-6} | 11.20×10^{-6} | Green |
| 30.50 | 2.151 | 2.896 | 11.15 | " |
| 24.97 | 1.636 | 2.235 | 11.12 | " |
| 20.00 | 1.166 | 1.642 | 11.09 | " |
| 13.82 | 0.585 | 0.883 | 10.89 | Blue |
| 7.35 | -0.026 | 0.105 | 10.50 | " |
| 3.82 | -0.359 | -0.299 | 10.28 | " |

TABLE III.

Variation in magnetic susceptibility of CuCl_2 dissolved in n-butyl alcohol.

| Comp. of the soln. | Magnetic susceptibility. Calc. | Obs. | χ (CuCl_2 solid). Calc. | Colour. |
|--------------------|-----------------------------------|------------------------|---|---------------|
| 15.11% | 0.294×10^{-6} | 0.484×10^{-6} | 10.43×10^{-6} | Green |
| 9.04 | 0.098 | 0.248 | 10.38 | " |
| 6.90 | -0.104 | 0.005 | 10.30 | " |
| 4.68 | -0.316 | -0.239 | 10.35 | " |
| 2.39 | -0.533 | -0.405 | 10.30 | " |
| 1.20 | -0.645 | -0.625 | 10.29 | Greenish blue |
| 0.405 | -0.720 | -0.725 | 7.584 | Blue |
| 0.122 | -0.747 | -0.750 | 6.716 | " |

TABLE IV.

Variation in magnetic susceptibility of CuCl₂ dissolved in n-propyl alcohol.

| Comp. of the soln. | Magnetic susceptibility. | | χ (CuCl ₂ solid). Calc. | Colour. |
|--------------------|--------------------------|------------------------|--|---------|
| | Calc. | Obs. | | |
| 15.11% | 0.666×10^{-6} | 0.993×10^{-6} | 10.87×10^{-6} | Green |
| 12.43 | 0.412 | 0.666 | 10.68 | " |
| 10.51 | 0.231 | 0.428 | 10.60 | " |
| 7.60 | -0.046 | 0.006 | 10.40 | " |
| 4.45 | -0.344 | -0.279 | 10.18 | " |
| 2.00 | -0.576 | -0.577 | 8.70 | Blue |
| 1.13 | -0.658 | -0.668 | 7.87 | " |
| 0.58 | -0.711 | -0.719 | 7.39 | " |

TABLE V.

Variation in magnetic susceptibility of CuCl₂ dissolved in ethyl alcohol.

| Comp. of the soln. | Magnetic susceptibility. | | χ (CuCl ₂ solid) Calc. | Colour. |
|--------------------|--------------------------|------------------------|---|---------|
| | Calc. | Obs. | | |
| 12.94% | 0.480×10^{-6} | 0.756×10^{-6} | 10.840×10^{-6} | Green |
| 10.40 | 0.239 | 0.447 | 10.670 | " |
| 8.16 | 0.030 | 0.185 | 10.620 | " |
| 4.79 | -0.291 | -0.135 | 10.315 | " |
| 2.40 | -0.517 | -0.482 | 10.180 | " |

TABLE VI.

Variation in magnetic susceptibility of CuCl₂ dissolved in methyl alcohol.

| Comp. of the soln. | Magnetic susceptibility. | | χ (CuCl ₂ solid) Calc. | Colour. |
|--------------------|--------------------------|------------------------|---|---------|
| | Calc. | Obs. | | |
| 32.10% | 2.348×10^{-6} | 2.675×10^{-6} | 9.738×10^{-6} | Green |
| 25.05 | 1.686 | 1.921 | 9.660 | " |
| 20.85 | 1.293 | 1.518 | 9.795 | " |
| 16.72 | 0.903 | 1.049 | 9.585 | " |
| 9.65 | 0.240 | 0.316 | 9.500 | " |
| 4.84 | -0.211 | -0.175 | 9.450 | " |
| 1.26 | -0.547 | -0.538 | 9.350 | " |

DISCUSSION.

In Tables II to IV are shown the results obtained by studying magnetic susceptibility of CuCl₂ in various solvents at different dilutions. Column 3 shows experimental values of magnetic susceptibility of the solutions. Column 4 gives the results calculated on the assumption that magnetic susceptibility of the solutions is the sum of the susceptibilities of the components.

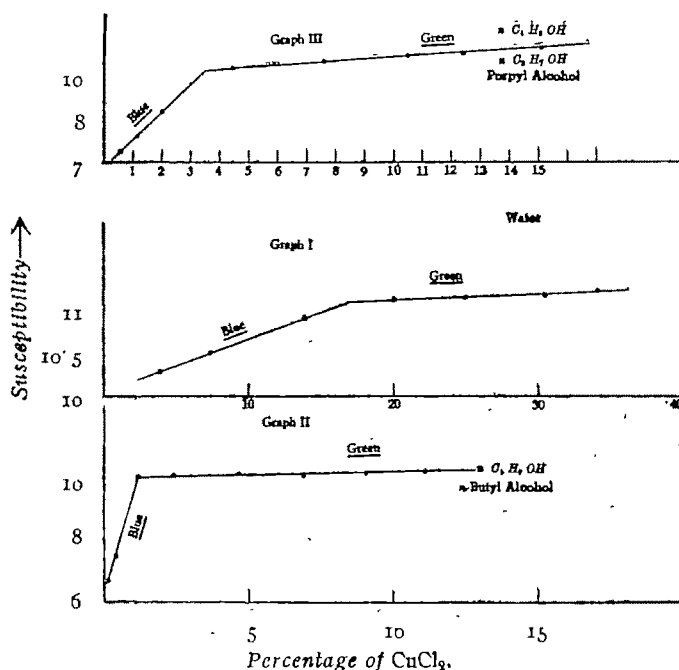
$$\chi_{\text{sol}} = C_s \chi_s + \chi_w (1 - C_s).$$

C_s is the amount of CuCl_2 in 1 g. of the solution, χ_{sol} , χ_s and χ_w are the magnetic susceptibilities of the solutions, solute and the solvent respectively.

We find that values of the mass susceptibility of the solution actually obtained and those calculated from the above formulae do not agree indicating that some change has taken place in solution.

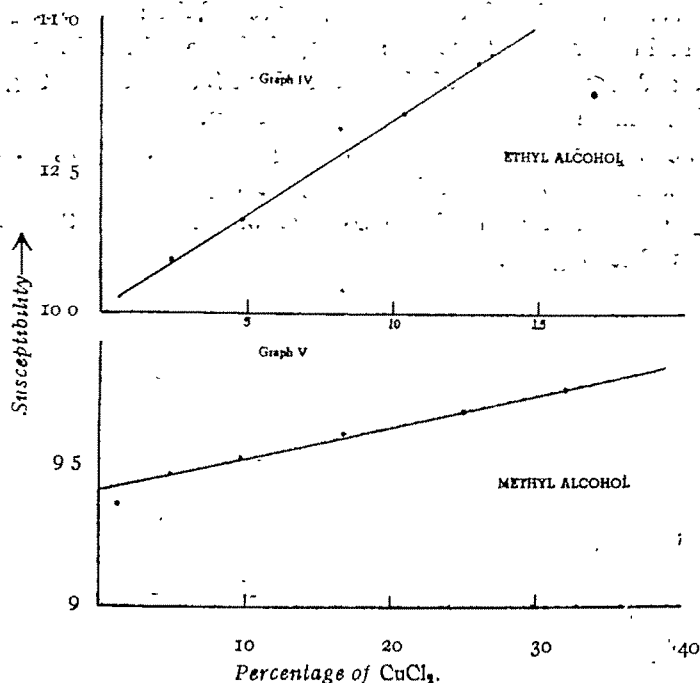
If we suppose that solvation takes place in solution, i.e. solute combines with the molecules of the solvent, the magnetic mass susceptibilities of CuCl_2 are not expected to change so much and moreover the deviations should have been regular.

FIG. I.



It has been shown by previous workers that the magnetic moment of the same ion in solution varies slightly with concentrations and to somewhat greater extent with nature of the solvent. A further support is lent to the above results by the recent work of S. Dutta (*Phil. Mag.*, 1934, iv, 16, 585) on studies on paramagnetism. He has shown that in the case of Co and Ni, the magnetic moments do not change very much when anhydrous salts pass from anhydrous state to the hydrated state. Ions and water dipoles surrounding the paramagnetic atom or ion are in the same relative position in two types of salts and give rise to the same field effect. In the case of coordination compounds, however, the crystalline field assumes an altogether different value due to interaction of new atomic grouping around the metallic ion.

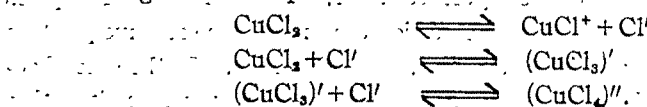
FIG. 2.



Actually we get a marked change in the susceptibility of CuCl_2 in these solvents which goes against the hydration theory of Wiederman. This change, however, can be explained on the basis of complex ion theory. There is a sudden change in susceptibility where there is a change in colour. This is better explained from the accompanying graphs (Fig. 1) in which the results of magnetic susceptibility are plotted against the concentrations. There is a sharp break in the graph accompanying the change of colour; in other words a transition takes place.

From Tables V and VI we find that changes in magnetic susceptibility are regular and there is no change of colour in the solutions. The curves are straight lines as is shown by graphs IV and V (Fig. 2.).

Thus it is clear that the colour change is associated with a break in susceptibility-concentration curve and the colour change is due to the formation or dissociation of complex ions of the type $(\text{CuCl}_3)'$ and $(\text{CuCl}_4)''$. These changes can be represented as



SOLUBILITIES OF WEAK ACIDS IN SALTS OF WEAK ACIDS:

By W. V. BHAGWAT, MAHABIRSINGH VARMA, AND H. G. HERMALKAR.

The solubilities of weak acids like benzoic acid and salicylic acid in sodium or potassium salts of various acids such as monochloroacetic acid, trichloroacetic acid, aminobenzoic acid, etc., have been determined. The observations are very similar to those made by Bhagwat and Doosag in case of other acids.

Bhagwat and Doosag (*J. Indian Chem. Soc.*, 1933, 10, 230) have determined the solubility of various weak acids in sodium salts of other weak acids. We have extended this work to various concentrations of salts of various weak acids such as monochloroacetic acid, trichloroacetic acid, benzenesulphonic acid, cinnamic acid, hippuric acid, etc., using benzoic acid and salicylic acid. From the results obtained and the graphs drawn following observations are made.

If we consider the solubilities of benzoic and salicylic acids in potassium salts of sulphanilic acid, phenylpropionic acid, glycollic acid, lactic acid, phenylacetic acid, *n*-butyric acid and *n*-propionic acid, we find that although the solubility of benzoic acid in pure water at the same temperature is greater than the solubility of salicylic acid, in potassium salts the solubility increases more rapidly for stronger salicylic acid than for benzoic acid. This is in accordance with the previous observations of Bhagwat and Doosag (*loc. cit.*). At a particular concentration of potassium salt, solubility of salicylic acid exceeds that of benzoic acid and then always remains greater than that of benzoic acid.

The solubility of benzoic acid and salicylic acid in the above mentioned salts shows a regularity except in the case of sulphanilic acid and phenylpropionic acid. The curves for the solubilities of benzoic and salicylic acids (not shown) in the case of phenylpropionic acid are somewhat irregular at low concentrations of potassium salts. After these concentrations they become regular. For sulphanilic acid, only the curve for the solubility of benzoic acid shows an irregularity at low concentrations. The concentrations of potassium salts at which the two curves meet are different for different acids and are in the following order: Phenylpropionic acid > *n*-butyric acid > propionic acid > sulphanilic acid > phenylacetic acid > lactic acid > glycollic acid.

The order of the dissociation constants of these acids are *n*-propionic acid (1.45×10^{-5}) < *n*-butyric acid (1.5×10^{-5}) < lactic acid (1.4×10^{-4}) < glycollic acid (1.4×10^{-4}).

From the results available it is concluded that the solubility of salicylic acid exceeds that of benzoic acid at lower concentrations in the salt solution of a stronger acid.

The solubilities of benzoic and salicylic acids in potassium salts of cinnamic and hippuric acids do not cut each other. However, in the case of cinnamic acid the two curves gradually approach each other. In other words, the solubility of salicylic acid increases more rapidly in the potassium salt than that of benzoic acid. Both the curves are similar and show a similar irregularity at low concentrations. Afterwards both become regular (curves not shown).

However, the curves of these acids in the potassium salt of hippuric acid are rather striking. Solubility of benzoic acid increases steadily, but the solubility of salicylic acid shows a break, and then rises only very slightly with increase in concentration of potassium salt of hippuric acid. Below this break, the solubility of salicylic acid increases more rapidly than that of benzoic acid and the two curves approach each other. However, beyond this point the curves go on diverging. In other words, the general rule that the solubility of a stronger acid increases at a greater rate than the solubility of weak acid in the same salt of an acid, seems to break down in case of this acid after certain point.

If we compare the solubility of a single acid in the solutions of potassium salts of different acids, it is observed that in general the solubility in the solution of the salt of a stronger acid is smaller, although deviations are common. Thus the order of the solubility of salicylic acid in salts of different acids is glycollic < lactic < *n*-butyric < *n*-propionic acid. The solubility curves in case of lactic acid and glycollic acid are rather striking. At low concentrations the solubilities are more or less the same. On increasing the concentration of potassium salt the solubility of salicylic acid in glycollic acid increases and then falls and finally becomes greater than the solubility in lactic acid.

Increase of concentration of potassium salt of hippuric and cinnamic acids does not seem to have an appreciable effect on the solubility of salicylic acid. The solubility in potassium phenylpropionate is smaller than in potassium hippurate for low concentrations. As the concentration is increased, the solubility of salicylic acid increases in potassium phenylpropionate. The order of solubility of salicylic acid in salts of different acids examined are as follows :—

n-Propionic acid > *n*-butyric acid > phenylacetic acid > lactic acid > glycollic acid > sulphanilic acid > phenylpropionic acid > hippuric acid > cinnamic acid.

The order of solubility of benzoic acid in potassium salt of the same acids is more or less the same except for hippuric acid in whose salt benzoic acid is more soluble than even in the salts of glycollic and lactic acids. Moreover, the curve (not shown) indicates that the solubility increases fairly rapidly as the concentration of the potassium salt of hippuric acid is increased. This is unlike the solubility of salicylic acid which changes only slightly with increase in concentration. Behaviour in potassium cinnamate is very similar to that of salicylic acid. The order of the solubility of benzoic acid in potassium salts of various acids is as follows :—

Benzenesulphonic acid < cinnamic acid < phenylpropionic acid < sulphanilic acid < glycollic acid < lactic acid < hippuric acid < phenylacetic acid < *n*-butyric acid < *n*-propionic acid.

The solubility of benzoic acid in sodium salts of monochloroacetic acid, trichloroacetic acid and *p*-aminobenzoic acid obeys the general rule, that the solubility is smaller in the salt of the stronger acid.

Solubility of both benzoic and salicylic acids in potassium salt of cinnamic acid shows an irregular curve at low concentrations. The solubility first increases, then decreases up to a point and again begins to increase regularly as the concentration of the potassium salt is increased. In potassium benzenesulphonate benzoic acid behaves similarly but there is one point of difference that solubility of benzoic acid decreases at first and then increases, afterwards becomes more or less constant and finally increases regularly as the concentration of potassium salt is increased.

Behaviour of potassium salt of 3 : 5-dinitrobenzoic acid is most peculiar. The solubility of benzoic acid first increases, becomes steady for a longer range, and then begins to fall as the concentration of the potassium salt is increased.

CALCULATION OF CRITICAL PRESSURE FROM BOILING POINT AND PARACHOR DATA.

BY M. S. TELANG.

The equation, $P_c = k \frac{T_b}{[P]}$, has been proposed for calculating the critical pressures from the boiling point and parachor data of various liquids.

Sugden (*J. Chem. Soc.*, 1924, **125**, 1177; "The Parachor and Valency", 1930, p. 31) has compared parachors and molecular critical volumes and has shown that the ratio of the parachor $[P]$ to the molecular critical volume (V_o) of a given compound has an almost constant value of 0.77 for all substances. Hence,

$$V_o = \frac{[P]}{0.77}.$$

According to Van der Waals, "at their critical points, the values of $P_o V_o / T_o$ should be the same for all substances" (*vide*, Young, "Stoichiometry," 1918, p. 207). So $P_o V_o / T_o = \tau$, where τ is a constant. This statement is true only when the molecules of an ordinary substance undergo no alteration during the process of liquefaction. When molecular association takes place as with acetic acid, alcohols, etc., the relation between temperature, pressure and volume becomes much more complex (*cf.* Young, *ibid.* p. 189),

The mean value of τ , as calculated from the data for twenty-five different substances (Young, *ibid.* p. 170) is 1625, when pressures and volumes are expressed in cm. and c.c. respectively. These values are incorporated in the following table.

Substituting for V_o and τ , the above equation becomes,

$$\frac{P_o \times \frac{[P]}{0.77}}{T_o} = 1625.$$

Rewriting, $P_o = 1625 \times 0.77 \times \frac{T_o}{[P]}.$

According to this equation,

$$P_o = 1251 \times \frac{T_o}{[P]},$$

if the known values of critical pressures are plotted against the corresponding values of the ratios of critical temperatures to the parachors, a straight line graph should be obtained with a slope of 1251.

CALCULATION OF CRITICAL PRESSURE FROM BOILING POINT, ETC. 367

| Substance | B. p. T_b . | $T_c/[P]$. | Critical pressure P_c | | $\frac{P_c V_c}{T_c} = r_c$. |
|----------------------|------------------|-------------|-------------------------|----------|-------------------------------|
| | | | obs. | calc. | |
| Diisobutyl | 382.2 | 1.594 | 1866 cm. | 2162 cm. | 1636 |
| n-Octane | 398.8 | 1.624 | 1873 | 2222 | 1612 |
| n-Heptane | 371.4 | 1.746 | 2043 | 2344 | 1654 |
| Diisopropyl | 331.1 | 1.852 | 2336 | 2447 | 1665 |
| n-Hexane | 342.0 | 1.880 | 2251 | 2471 | 1627 |
| isoPentane | 301.0 | 2.001 | 2502 | 2551 | 1668 |
| n-Pentane | 309.2 | 2.042 | 2510 | 2620 | 1654 |
| Methyl isobutyrate | 365.3 | 2.130 | 2574 | 2808 | 1613 |
| Ethyl propionate | 372.0 | 2.144 | 2522 | 2263 | 1590 |
| Propyl acetate | 374.6 | 2.145 | 2523 | 2855 | 1585 |
| Methyl butyrate | 375.8 | 2.183 | 2606 | 2888 | 1598 |
| Ether | 307.6 | 2.205 | 2706 | 2836 | 1634 |
| Hexamethylene | 353.9 | 2.362 | 3028 | 2952 | 1681 |
| Ethyl acetate | 350.2 | 2.410 | 2888 | 3148 | 1580 |
| Methyl propionate | 352.7 | 2.458 | 3003 | 3190 | 1595 |
| Propyl formate | 353.9 | 2.489 | 3046 | 3196 | 1612 |
| Carbon tetrachloride | 349.8 | 2.530 | 3418 | 3104 | 1697 |
| Iodobenzene | 461.5 | 2.574 | 3391 | 3214 | 1650 |
| Chlorobenzene | 405.0 | 2.595 | 3393 | 3447 | 1652 |
| Bromobenzene | 429.0 | 2.606 | 3391 | 3949 | 1638 |
| Fluorobenzene | 358.2 | 2.613 | 3391 | 3265 | 1643 |
| Benzene | 353.2 | 2.722 | 3640 | 3342 | 1660 |
| Methyl acetate | 330.1 | 2.846 | 3521 | 3617 | 1581 |
| Ethyl formate | 327.3 | 2.867 | 3554 | 3603 | 1601 |
| Methyl formate | 304.9 | 3.527 | 4503 | 4309 | 1590 |

Mean 1625

It is observed that the mean value of $T_c/T_b = 1.56$, where T_b is the boiling point of a substance. So, $T_c = 1.56 T_b$. Substituting this value of T_c in the above equation,

$$P_c = 1251 \times 1.56 \times \frac{T_b}{[P]} = 1952 \times \frac{T_b}{[P]},$$

or
$$P_c = k \cdot \frac{T_b}{[P]}$$

where k is a constant, the magnitude of which depends upon the units employed in expressing the pressures and volumes.

Expressing in a general manner, *the critical pressure of a substance is given by the ratio of its boiling point to its parachor multiplied by a constant.*

The applicability of this equation can be well illustrated by the values calculated for twenty-five different substances given. It can be observed from the table that the calculated values are in quite good agreement with the observed values (due to Young, *loc. cit.*) considering the fact that various approximations are employed in deducing the equation.

These calculations, besides lending further support to Sugden's theory that the parachor is really equivalent to a molecular volume, are useful for quickly estimating the critical pressures of various substances without actually performing any experiment regarding the critical phenomena. Further, this calculation is a rough guide in the actual determination of critical pressure which is by no means easily observable; the boiling point and parachor data are readily available from literature.

Some of the deviations observed can be attributed to the deviation of the actual value of T_c/T_b from the mean value of 1.56. More correct results may be obtained if the following corrections are introduced :

- (i) For the higher members of the homologous series, $T_c/T_b = 1.45$.
- (ii) For elements, like chlorine, bromine, oxygen, argon etc.,
 $T_c/T_b = 1.75$.

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PHOTOREDUCTION OF URANYL NITRATE BY TARTARIC ACID

BY T. L. RAMA CHAR.

Measurements of the optical rotation of mixtures of uranyl nitrate and tartaric acid show that a complex compound is formed in solution. The photoreduction of this complex has been studied in the visible and ultraviolet regions.

Ghosh and Mitter (*J. Indian Chem. Soc.*, 1927, **4**, 353) found that complex formation takes place between uranyl salt and various organic acids like tartaric, lactic, mandelic, etc. It is well known that uranyl salts are photochemically reduced by these acids: U^6 (yellow) \rightarrow U^4 (green or blue).

Complex Formation.

When uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, is added to *d*- or *l*-tartaric acid, the rotatory power of tartaric acid is enhanced. Measurements of the rotation of tartaric acid-uranyl mixtures, keeping the concentration of tartaric acid constant, gave maximum rotations for mixtures of the composition H_2T 4-uranyl (where T =tartrate ion). Assuming that in these mixtures complex formation is complete i.e., concentration of complex = conc. of H_2T , the dissociation constant of the complex

$$K = \frac{[\text{Complex}]}{[H_2T\text{-complex}] \times [\text{uranyl complex}]} \quad \dots (i)$$

was calculated as follows:

The observed rotation for any mixture is given by

$$\begin{aligned} \text{Observed rotation} &= (\text{molecular rotation of complex}) \times [\text{complex}] \\ &+ (\text{molecular rotation of free } H_2T) \times [H_2T] \quad \dots (ii) \end{aligned}$$

For mixtures giving maximum rotations, conc. of complex = conc. of H_2T , and we have from equation (ii),

$$\text{Observed rotation} = (\text{mol. rotation})_{\text{complex}} \times [H_2T],$$

$$\text{i.e., } (\text{mol. rotation})_{\text{complex}} = \frac{\text{observed maximum rotation for mixture}}{[H_2T]} \quad (iii)$$

similarly for free tartaric acid we have

$$(\text{Mol. rotation})_{\text{free } H_2T} = \frac{\text{observed rotation for free } H_2T}{[H_2T]} \quad \dots (iv)$$

From the observed rotation of any mixture, the concentration of the complex can be calculated from equations (ii), (iii) and (iv) by knowing the rotation of free tartaric acid and the maximal rotation for a set of mixtures. The dissociation constant K can then be calculated by substitution in equation (i).

The changes in the rotation of the mixtures were followed with a Winkel-Zeiss triple-field polarimeter which gave readings correct to 0.01° . The chemicals used were Merck's samples; the tartaric acids were recrystallised before use. 'Conductivity water' was used for preparing the solutions. The value of K was calculated by measuring the rotations of 3 sets of mixtures, and the results are given below.

TABLE I.

Length of solution = 2.5 cm. $\lambda = 5893\text{\AA}$. Temp. = 25° .

| Conc. of $d\text{-H}_2\text{T}$. | Conc. of uranyl. | Observed rotation. | Conc. of complex. | K . |
|-----------------------------------|------------------|--------------------|-------------------|-------|
| 0.250M | 1.000M | +0.28° | 0.250M | |
| " | 0.500 | +0.24 | 0.187 | 9.5 |
| " | 0.250 | +0.21 | 0.140 | 11.6 |
| " | 0.125 | +0.17 | 0.078 | 9.6 |
| " | 0.071 | +0.15 | 0.047 | 9.7 |
| " | 0.031 | +0.12 | — | — |
| " | 0.016 | +0.12 | — | — |
| " | — | +0.12 | — | — |
| 0.125 | 0.500 | +0.14 | 0.125 | |
| " | 0.250 | +0.11 | 0.078 | 9.6 |
| " | 0.062 | +0.08 | 0.031 | 10.6 |
| " | 0.016 | +0.06 | — | — |
| " | 0.004 | +0.06 | — | — |
| " | — | +0.06 | — | — |
| 0.062 | 0.250 | +0.07 | 0.062 | |
| " | 0.125 | +0.05 | 0.031 | 10.6 |
| " | 0.050 | +0.04 | 0.016 | 10.2 |
| " | 0.031 | +0.03 | — | — |
| " | 0.008 | +0.03 | — | — |
| " | — | +0.03 | — | — |

Mean value = 10.2

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The results show that fairly concordant values are obtained for the dissociation constant K . As the concentration of uranyl is decreased, the concentration of complex in the mixture decreases; the rotation of the mixture also decreases until in the limit it is equal to that of free tartaric acid. The sign of the rotation of the complex is the same as that of tartaric acid. *l*-Tartaric acid forms complexes whose rotations are equal in magnitude but opposite in sign to those of *d*-tartaric acid.

Photoreduction.

The complex formed by the addition of uranyl nitrate to tartaric acid is photochemically reduced in the visible as well as in the ultraviolet; tartaric acid is oxidised and the uranyl salt is reduced to the uranous state, the colour change being from yellow to green. This reaction has been studied in the ultraviolet, violet and blue regions.

The experimental arrangement for studying the photo-reaction was the same as that described in a previous paper (Rama Char, *J. Indian Chem. Soc.*, 1941, 18, 507). The reaction was followed by the estimation of the reduced uranium. A known volume of an excess of standard permanganate was added in sulphuric acid solution to convert all the reduced uranium to the uranyl state, and the excess of permanganate was titrated iodimetrically. The whole process was carried out in an atmosphere of carbon dioxide to prevent oxidation of the uranous salt by air. There is no dark reaction for the mixtures studied, and the photochemical reaction is zero-molecular with respect to uranyl (U^6). Table II gives the effect of varying the concentration of the reactants on the velocity of the photoreduction in the ultraviolet. dx/dt refers throughout to the number of g. mols. transformed per minute. Unless otherwise stated, *d*-tartaric acid has been used.

Reaction in the Ultraviolet.

TABLE II.

$\lambda = 3130\text{\AA}$ (Chance Bros.). $p_H = 0.9$ to 1.3 . Temp. = 28° .

$$(dx/dt)_{\text{calc.}} = 20.52 \times 10^{-8} \cdot I_{\text{abs.}} \times \frac{[H_2T]}{0.2 + [H_2T]} \text{ (for all wave-lengths).}$$

| Conc. of H_2T . | Conc. of uranyl. | $I_{\text{abs.}}$ | $dx/dt \times 10^4$ | |
|-------------------|------------------|-------------------|---------------------|-------|
| | | | obs. | calc. |
| 0.500M | 0.500M | 7270 ergs | 10.65 | 10.65 |
| 0.333 | 0.333 | 6570 | 8.60 | 8.45 |
| 0.250 | 0.250 | 6230 | 7.10 | 7.10 |
| 0.167 | 0.167 | 5710 | 5.45 | 5.35 |
| 0.125 | 0.125 | 5190 | 4.10 | 4.10 |

TABLE II (contd.).

| Conc. of H_2T . | Conc. of uranyl. | $I_{abs.}$ | obs $\frac{dx}{dt} \times 10^4$. | calc |
|-------------------|------------------|------------|-----------------------------------|-------|
| 0.500M | 0.500M | 7270 ergs | 10.65 | 10.65 |
| 0.250 | " | " | 7.50 | 7.15 |
| 0.125 | " | " | 5.10 | 5.00 |
| 0.063 | " | " | 3.05 | 3.05 |
| 0.500 | 0.250 | 6230 | 9.10 | 9.15 |
| 0.250 | " | " | 7.10 | 7.10 |
| 0.125 | " | " | 4.85 | 4.90 |
| 0.063 | " | " | 3.00 | 3.05 |
| 0.500 | 0.125 | 5190 | 7.65 | 7.60 |
| 0.250 | " | " | 5.80 | 5.80 |
| 0.125 | " | " | 4.10 | 4.10 |
| 0.063 | " | " | 2.50 | 2.55 |

The velocity of the reaction decreases with decrease in equimolar concentration. Decrease in the concentration of tartaric acid, keeping the concentration of uranyl constant, results in a decrease in the velocity. Table III shows that, for the same mixture, the velocity of the reaction is directly proportional to the intensity of the light absorbed.

TABLE III.

$\lambda = 3130 \text{ \AA}$. $p_H = 0.9$ to 1.1 . Temp. = 28° .

| Conc. of H_2T . | Conc. of uranyl. | $I_{abs.}$ | $\frac{dx}{dt} \times 10^4$. |
|-------------------|------------------|------------|-------------------------------|
| 0.50M | 0.50M | 7270 ergs | 10.65 |
| " | " | 4670 | 6.90 |
| " | " | 3290 | 4.85 |
| 0.25 | 0.25 | 6230 | 7.10 |
| " | " | 3980 | 4.50 |
| " | " | 2840 | 3.25 |

PHOTOREDUCTION OF URANYL NITRATE BY TARTARIC ACID 373

Reaction in the Violet.—Table IV gives the effect of varying the concentration of the reactants on the velocity of the reaction in the violet region. Table V gives the effect of varying I_{abs} .

TABLE IV.

$\lambda = 4060\text{\AA}$ (Zeiss monochromat). $p_{\text{H}} = 0.9$ to 1.2 . Temp. = 28° .

| Conc. of H_2T . | Conc. of uranyl. | I_{abs} . | obs. $\frac{dx}{dt} \times 10^4$. | calc. |
|---------------------------------|------------------|--------------------|------------------------------------|-------|
| 0.500M | 0.500M | 7700 ergs. | 11.30 | 11.30 |
| 0.333 | 0.333 | 7000 | 9.40 | 9.00 |
| 0.250 | 0.250 | 6570 | 7.50 | 7.50 |
| 0.167 | 0.167 | 5530 | 5.30 | 5.15 |
| 0.125 | 0.125 | 4500 | 3.50 | 3.55 |
| 0.500 | 0.500 | 7700 | 11.30 | 11.30 |
| 0.250 | " | " | 8.60 | 8.80 |
| 0.125 | " | " | 6.15 | 6.30 |
| 0.063 | " | " | 3.70 | 3.75 |
| 0.500 | 0.250 | 6570 | 9.55 | 9.65 |
| 0.250 | " | " | 7.50 | 7.50 |
| 0.125 | " | " | 5.10 | 5.20 |
| 0.063 | " | " | 3.20 | 3.20 |

TABLE V.

$\lambda = 4060\text{\AA}$. $p_{\text{H}} = 0.9$ to 1.1 . Temp. = 28° .

| Conc. of H_2T . | Conc. of uranyl. | I_{abs} . | $\frac{dx}{dt} \times 10^4$. |
|---------------------------------|------------------|--------------------|-------------------------------|
| 0.500M | 0.500M | 7700 ergs. | 11.30 |
| " | " | 5620 | 8.00 |
| " | " | 3980 | 5.75 |
| 0.250 | 0.250 | 6570 | 7.50 |
| " | " | 4840 | 5.55 |

The general nature of the reaction in the violet is the same as that in the ultraviolet. For the same mixture, the velocity is proportional to I_{abs} .

Reaction in the Blue.—Tables VI and VII give the results obtained for the photoreduction in the blue region. They are of the same type as those obtained in the ultraviolet and violet regions. The velocity of the reaction is proportional to the intensity of the blue light absorbed.

TABLE VI.

$\lambda = 4360\text{\AA}$ (Zeiss monochromat). $p_H = 0.9$ to 1.2 . Temp. = 28° .

| Conc. of H_2T . | Conc. of uranyl. | $I_{\text{abs.}}$ | $dx/dt \times 10^4$. | |
|-------------------|------------------|-------------------|-----------------------|------|
| | | | obs | calc |
| 0.500M | 0.500M | 4500 ergs. | 6.60 | 6.60 |
| 0.333 | 0.333 | 4150 | 5.50 | 5.30 |
| 0.250 | 0.250 | 3770 | 4.30 | 4.30 |
| 0.167 | 0.167 | 3370 | 3.00 | 3.10 |
| 0.125 | 0.125 | 2850 | 2.20 | 2.25 |
| 0.500 | 0.500 | 4500 | 6.60 | 6.60 |
| 0.250 | " | " | 5.00 | 5.10 |
| 0.125 | " | " | 3.50 | 3.55 |
| 0.063 | " | " | 2.20 | 2.20 |
| 0.500 | 0.250 | 3770 | 5.60 | 5.75 |
| 0.250 | " | " | 4.30 | 4.30 |
| 0.125 | " | " | 3.00 | 3.00 |
| 0.063 | " | " | 1.70 | 1.85 |

TABLE VII.

$\lambda = 4360\text{\AA}$. $p_H = 0.9$ to 1.1 . Temp. = 28° .

| Conc. of H_2T | Conc. of uranyl. | $I_{\text{abs.}}$ | $dx/dt \times 10^4$. |
|-----------------|------------------|-------------------|-----------------------|
| 0.50M | 0.50M | 4500 ergs | 6.6 |
| " | " | 2850 | 4.1 |
| 0.25 | 0.25 | 3770 | 4.3 |
| " | " | 2390 | 2.7 |

Reaction with d-, l- and r-Acids.—Some experiments were also carried out with l- and racemic-tartaric acids as reductants. The results given in Table VIII below show that there is no difference in the velocity of the photoreduction with these reductants in all the wave-lengths studied.

TABLE VIII.

 $p_H = 0.9$ to 1.1. Temp. = 28°.

| Wave-length | Conc. of H_2T . | Conc. of uranyl. | $I_{abs.}$ for all complexes. | $d-H_2T$. | $dx/dt \times 10^4$. $l-H_2T$. | $r-H_2T$. |
|-------------|-------------------|------------------|-------------------------------|------------|-------------------------------------|------------|
| 3130Å | 0.50M | 0.50M | 7270 ergs. | 10.65 | 10.60 | 10.60 |
| " | 0.25 | 0.25 | 6230 | 7.10 | 7.10 | 7.15 |
| 4060 | 0.50 | 0.50 | 7700 | 11.30 | 11.30 | 11.25 |
| " | 0.25 | 0.25 | 6570 | 7.50 | 7.45 | 7.50 |
| 4360 | 0.50 | 0.50 | 4500 | 6.60 | 6.55 | 6.60 |
| " | 0.25 | 0.25 | 3770 | 4.30 | 4.35 | 4.30 |

Table IX gives the quantum efficiency of the photo-process in the ultraviolet, violet and blue regions.

TABLE IX.

 $p_H = 0.9$ to 1.2. Temp. = 28°.

| Conc. of H_2T . | Conc. of uranyl. | Quantum efficiency (γ). | | |
|-------------------|------------------|----------------------------------|--------|--------|
| | | 3130Å. | 4060Å. | 4360Å. |
| 0.500M | 0.500M | 4.7 | 3.6 | 3.4 |
| 0.250 | 0.250 | 3.6 | 2.8 | 2.6 |
| 0.125 | 0.125 | 2.5 | 2.1 | 1.8 |

The value of γ decreases with increasing wave-length of the radiation, and for the same wave-length, it decreases with decreasing concentration of the complex.

Reaction in Circularly Polarised Light.—The influence of d - and l -circularly polarised light on the velocity of the photoreduction in the visible and in the ultraviolet regions was studied. Circularly polarised light was obtained by the combination of a polaroid and a Fresnel's rhomb for the visible, and by the combination of a Glans polarising prism and a Carl-Zeiss quarter-wave plate for the ultraviolet region. The results obtained are given below.

TABLE X.

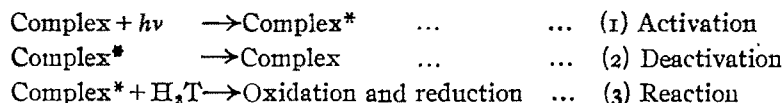
Conc. of $H_2T = 0.50M$. Conc. of uranyl = 0.50M. $p_H = 0.9$, Temp. = 28°.

| Radiation. | Polarised light. | $I_{abs.}$ for all complexes. | $d-H_2T$. | $dx/dt \times 10^5$. $l-H_2T$. | $r-H_2T$. |
|---------------|------------------|-------------------------------|------------|-------------------------------------|------------|
| 3130Å | d -circular | 1040 ergs. | 7.2 | 7.2 | 7.2 |
| | l " | " | 7.2 | 7.3 | 7.1 |
| Whole visible | d " | 1120 | 14.6 | 14.6 | 14.7 |
| | l " | " | 14.5 | 14.5 | 14.8 |

There is no difference in the velocity of the reaction in *d*- and *l*-light, either visible or ultraviolet. For the same kind of polarised light, there is no difference in the velocity with complexes of *d*-, *l*- or racemic-acids.

DISCUSSION.

The following mechanism can explain the main features of the photo-reduction of the uranyl nitrate-tartaric acid complex :



If k_1 , k_2 , and k_3 are the velocity constants for the processes (1), (2) and (3) respectively, we have for the velocity of the reaction the equation,

$$dx/dt = I_{\text{abs}} \times \frac{k_1 \times [\text{H}_2\text{T}]}{(k_2/k_3) + [\text{H}_2\text{T}]}$$

i.e., $I_{\text{abs}} \left/ \frac{dx}{dt} \right.$ when plotted against $1/\text{conc. of H}_2\text{T}$, should give a straight line, as is actually the case. There is good agreement between the observed values of the velocity and those calculated from the above equation, wherein k_1 and k_2/k_3 have the values given in the above tables.

The author wishes to express his thanks to Prof. J. C. Ghosh for his kind interest in this work.

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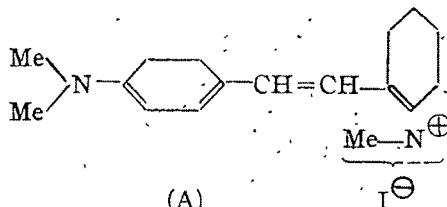
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THE CYANINE DYES OF THE PYRIDINE SERIES. PART III.

By M. Q. DOJA AND DHANUSDHAR PRASAD.

An attempt has been made to synthesise a uniformly powerful photographic sensitiser, which will be useful in the manufacture of "panchromatic" plates. With this end in view *p*-diethylaminobenzaldehyde has been condensed respectively with α -picoline-methiodide, -ethiodide, *n*-propyl iodide and *n*-butyl iodide and the dyestuffs thus obtained examined for their chemical, dyeing, optical, and photographic properties.

Mills and Pope (*J. Chem. Soc.*, 1922, **121**, 946) prepared an important member of the pyridine series of cyanine dyes, 2-*p*-dimethylaminostyrylpyridine-methiodide (A).



This substance possesses the unique property of showing almost uniform sensitiveness to the light of all wave-lengths from the blue to about $\lambda 5600$, and is thus free from the defect of failing to sensitise photographic plates for a short region in the bluish green, which so frequently occurs with sensitisers for the red region of the spectrum. It is this latter drawback which has necessitated the use of *two* sensitisers, a "red" and a "green" one, in the manufacture of plates, uniformly sensitive to all wave-lengths from the blue to the red end of the spectrum—the so-called "panchromatic" plates. If (A) could be made to sensitise further into the red, it may be possible to use only *one* sensitiser in the preparation of panchromatic plates. Among the photographic sensitisers, belonging to the cyanine dye groups, an increase in the molecular weight of a compound is known to produce a shift of the maximum of extra-sensitisation towards the red (Hamer, *J. Chem. Soc.*, 1929, 2598; *ibid*, 1930, 995). In the molecule of (A), without affecting its essential structural features, this increase can be effected in several ways. One method would be to change the anion. This, however, is not expected to be helpful, because it has been shown (Kiprianov and Schusser, *Proc. Charkov State Univ*, 1936, **4**, 49; Hamer, *Phot. J.*, 1929, **53**, 414) that a change in the anion of a cyanine dyestuff has no influence on its sensitising character. Another method would be to increase the size of the alkyl radical attached to the quaternary nitrogen atom. This has been tried (Doja and Prasad, *J. Indian Chem. Soc.*, 1942, **19**, 125). Molecules of (A) containing ethyl, propyl and butyl in place of methyl of the quaternary nitrogen atom, have been synthesised.

As expected, the butyl compound does not push the band of extra sensitisation farther towards the red, but not sufficiently far to replace the "red" sensitisers used in the manufacture of panchromatic plates. Attempts to introduce alkyl radicles, larger than butyl, failed probably due to steric influences (*cf.* Mills and Hamer, *J. Chem. Soc.*, 1922, 121, 2008). A third method of enhancing the molecular weight of (A), would be to substitute the methyl on the tertiary nitrogen atom by larger radicles. The present paper deals with the preparation and properties of such compounds.

p-Diethylaminobenzaldehyde (supplied by Messrs Eastman Kodak Company of Rochester, New York) has been condensed respectively with α -picoline-methiodide, -ethiodide -*n*-propyl iodide and -*n*-butyl iodide, yielding dyestuffs possessing the usual "cyanine" characteristics. The crystals are pleochroic and exhibit characteristic reflexes. They are easily soluble in methyl alcohol, ethyl alcohol, water and acetic acid, slightly soluble in ligroin, and insoluble in ether, benzene and chloroform. The solubility of these compounds increases with decrease in molecular weight, thus the methiodide is the most soluble in the series. The yield of all the four compounds is high and compares favourably with the yields of the corresponding condensation products with *p*-dimethylaminobenzaldehyde (Doja and Prasad, *loc. cit.*). For a good yield, however, it is essential that the constituents should be carefully dried before use, and even during condensation no moisture should be allowed to enter the reaction vessel. In contrast with those of the corresponding *p*-dimethylamino compounds (*loc. cit.*), the melting points of these substances do not show any regularity as we ascend or descend the series. The melting points together with the other characteristics of the crystals are recorded in Table I.

TABLE I.

| Compounds. | Crystalline form. | M.p. | Colour by reflected light. | Colour through transmitted light. | Pleochroism | | Reflex. |
|------------|------------------------------|------|----------------------------|-----------------------------------|--|------------------------------------|-----------------------------------|
| | | | | | Colour of light in one position of polariser | Colour after rotation through 90°. | |
| (P) | Flattened needles | 241° | Light mauve | Ruby-red (in thin sheets orange) | Deep pink | Nearly opaque | Strong scintillating light - blue |
| (Q) | Thin small felted needles | 205° | Vermilion red | Reddish orange | Orange-yellow (very weak) | Rose | Medium bluish white |
| (R) | Fine long needles | 235° | Scarlet | Deep rose red | Rose-red | Reddish black | Strong arc blue |
| (S) | Cluster of tetragonal prisms | 244° | Reddish violet | Claret red | Orange-yellow | Dull orange | Strong shining violet |

In Tables I—VII (P), (Q), (R), (S) refer respectively to the methoiodide, ethoiodide, propyl iodide and butyl iodide of the dye.

Both aqueous and alcoholic solutions of these dyestuffs are orange-yellow in colour, the former possessing a pronounced reddish tinge, which is most marked in the lightest member, the methoiodide, and least so in the heaviest member, the butyl iodide. The relative intensity of transmitted light for equivalent solutions in rectified spirit of the four compounds, as measured by a Duboscq colorimeter, is given in Table II. It is noteworthy that the order of relative intensity is the same in both the *p*-dimethylamino (Doja and Prasad, *loc. cit.*) and the *p*-diethylamino compounds: -Ethoiodide> methoiodide> -propyl iodide> -butyl iodide.

TABLE II.

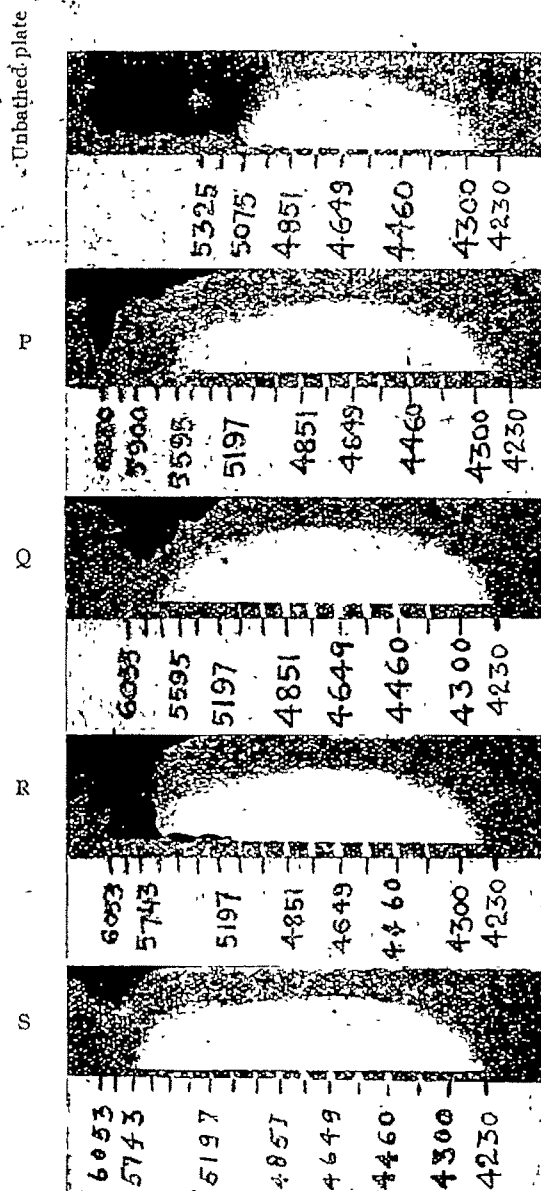
| | Depth of the solution of | | | |
|--------------------|----------------------------------|----------------------------------|----------------------------------|--|
| (P) | (Q) | (R) | (S) | |
| 12 | 10'1 } 10'2 } 10'1 } 10'13 | 12'2 } 12'2 } 12'3 } 12'23 | 15'0 } 15'1 } 15'0 } 15'03 | |
| 18 | 16'2 } 16'1 } 16'2 } 16'16 | 18'3 } 18'3 } 18'2 } 18'26 | 21'1 } 21'1 } 21'1 } 21'10 | |
| Relative intensity | 1'18 } 1'15 } 1'16 | 0'98 } 0'98 } 0'98 | 0'79 } 0'85 } 0'82 | |

TABLE III.

| Name and vol. of the dye soln. used. | Volume of N/100-HCl required in c. c. | | |
|--------------------------------------|---------------------------------------|---------------------------|--------------------------|
| | Alcoholic solution | Aqueous solution. | |
| | | Light lemon yellow colour | Complete decolourisation |
| (P)—2 c.c. | 3'9 3'95 4'0 | 1'1 1'15 1'2 | 22'1 22'10 22'1 |
| (Q)—2 c.c. | 4'2 4'15 4'1 | 1'2 1'20 1'2 | 22'2 22'25 22'3 |
| (R)—2 c.c. | 4'3 4'30 4'3 | 1'5 1'55 1'6 | 7'7 7'70 7'7 |
| (S)—2 c.c. | 4'2 4'20 4'2 | 1'5 1'50 1'5 | 8'5 8'50 8'5 |

Mills and Pope (*Phot. J.*, 1920, **44**, 255) have observed that alcoholic

FIG. I.



solutions of certain cyanine dyes are more resistant to decolourisation by mineral acids than their aqueous solutions. With the set of dyes which we have prepared such is not the case. For the same volume, the aqueous solution requires a much larger quantity of the dilute mineral acid for the complete discharge of colour, than the alcoholic solution. In the case of the aqueous solutions, the first c.c. has a rapid discharging effect; afterwards the light lemon-yellow colour of the solution becomes very resistant, and is not completely discharged until after the addition of a comparatively large volume of acid. The alcoholic solutions on the other hand, behave normally. From the figures given in Table III, it appears that in aqueous solution, the methiodide and the ethiodide form one similar pair and the propyl and butyl iodides another. In alcoholic solution, all the four compounds behave more or

less alike. Silk, wool and cotton have been dyed with these in the same way as described in an earlier communication (Doja and Prasad, *loc. cit.*). The first two develop orange shades, and the third a chocolate brown

colour, the reddish tinge of all of which deepened with increasing molecular weight of the dye. Although some of the shades are very pretty, none of them is fast to sunlight or soap washing, the shades produced together with other relevant data are summarised in Table IV.

TABLE IV.

| Compound | Silk | Colour produced on Wool. | Cotton. |
|----------|----------------|--------------------------|-------------------|
| (P) | Orange-yellow | Bright orange | Light chocolate |
| (Q) | Orange | Rich orange | Chocolate |
| (R) | Reddish orange | Deep orange | Chocolate-brown |
| (S) | Orange-red | Orange-red | Reddish chocolate |

Remarks:

1. Cotton and wool were dyed both from acid and neutral baths, the former always producing a weaker shade
2. Silk was dyed from weakly acid baths only
3. Shades produced on wool, showed greatest (fading) resistance towards sunlight

Fig. 1 gives the sensitisation spectra of these dyestuffs, photographed as before (Doja and Prasad, *loc. cit.*), except that the solution this time is 1 : 30,000, and the time of development four minutes. It will be seen that the chief characteristic of these spectrographs is the uniformly high intensity of the bands of extra-sensitisation. There is no gap, the induced

TABLE V.

| Compound. | Total range of sensitisation. | Range of uniformly intense sensitisation. | Sensitisation | |
|-----------|-------------------------------|---|---------------|-------|
| | | | Max. | Min. |
| (P) | 4250-5650Å | 4400-5450Å | 5350Å | 5050Å |
| (Q) | 4200-5750 | 4350-5500 | 5400 | 5000 |
| (R) | 4250-5750 | 4400-5650 | 5500 | 5050 |
| (S) | 4200-5800 | 4350-5750 | 5550 | 5000 |

sensitisation bands merging completely into the normal sensitivity of the plate. As is to be expected, the gradual increase in the molecular weight produces a regular shift of the sensitisation maxima (Table V) towards the red end of the spectrum, the butyl iodide of the dye being the heaviest, produces the maximum shift. On the whole, these new dyes obtained from *p*-diethylaminobenzaldehyde, are better sensitisers than the corresponding ones derived from *p*-dimethylaminobenzaldehyde (Doja and Prasad, *loc. cit.*).

The fluorescence of weak solutions (1:50,000 in 90% alcohol) of these compounds is given in Table VI. These have been determined in the same way as described by Doja (*J. Indian Chem. Soc.*, 1940, **17**, 348).

TABLE VI.

Colour of the fluorescent beam.

| Wallace colour filter number | (P). | (Q). | (R). | (S). |
|---------------------------------|------------------------|-------------------|--------------------|----------------|
| 1 | Weak red | Weak red | Weak red | Red |
| 2 | Crimson red | Claret red | Flaming red | Flaming red |
| 3 | Pink | Rose red | Weak pink | Light scarlet |
| 4 | Reddish yellow | Weak orange | Orange | Yellowish red |
| 5 | Weak yellow | Lemon-yellow | Weak turmeric | Yellow |
| 6 | Weak yellow | Yellow | Lemon-yellow | Weak yellow |
| 7 | Grass green | Light green | Bottle green | Light green |
| 8 | Weak green | Weak bottle green | Weak emerald green | Weak green |
| 9 | Very weak bluish green | Light absorbed | Light absorbed | Light absorbed |
| 10 | Weak orange | Very weak orange | Weak orange | Weak orange |

TABLE VII.

| (Q) crystal- lized from | Nature of crystals. | Reflex. | Pleochroism | | | |
|----------------------------|---|----------------------------|---------------------------------|--|---|--|
| | | | Colour by reflected light | Colour through transmitted light. | Colour in 1st posi- tion of polariser. | Colour in position at 90° to 1st. |
| Methyl alcohol | Mixture of rhombs and needle clusters | Weak greenish blue | Maroon | Ruby red | Orange-red | Dull red |
| Ethyl alcohol | Well de- veloped large tetragonal crystals | Strong grass green | Deep amethyst | Orange- red | Deep red (weak) | Orange- yellow |
| n-Propyl alcohol | Thin small felted needles | Medium bluish white. | Vermilion red | Reddish orange | Orange- yellow (very weak) | Rose |
| n-Butyl alcohol | Beautiful mica like glisten- ing blunt needles | Strong bluish white | Deep vermillion | Brownish yellow | Light yellow | Deep brown |
| n-Amyl alcohol | Large aggre- gates of irre- gular crystals | Weak bluish white | Signal red | Claret red | Brownish yellow (weak) | Reddish brown |

Some difficulty has been encountered in the purification by recrystallisation of the ethiodide (Q). Alcohols are known to be good crystallising solvents for cyanine dyes, the five alcohols, methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl, are, therefore, the first in which suitable conditions for the crystallisation of (Q) have been studied. It is found that the dye comes out best from a concentrated solution in *n*-propyl alcohol, when rapidly cooled the yield is high, the crystals are pure and the manipulation smooth. Although the five samples of (Q), obtained from the five different alcohols, are chemically identical without any solvent of crystallisation and possess the same m.p. 205° , they differ in their crystalline form and optical properties. These are recorded in Table VII.

A sample of (Q), recrystallised from *n*-butyl alcohol, exhibits another unusual characteristic. When moistened with water the deep vermilion crystals turn permanently into light brick red, and the original colour does not return even after complete drying of the crystals. None of the other samples exhibits this colour change.

The ethiodide of the series (Q), appears to behave in a way different from the others. It has a low melting point, 205° , (not of the same order as the others), it forms relatively the most intensely coloured solution (relative Intensity, 1.16), it has a very weak pleochroism, is difficult to purify, and in its preparation the constituents have to be heated for a longer period (16 hours) than in other cases.

This uncommon behaviour of an ethiodide in a series of cyanine dyes is not quite unknown. Pope and Mills (*Phot. J.*, 1920, **44**, 256) noticed that whereas carbocyanine ethiodide is a powerful photographic sensitiser, the other members of the series do not possess this property to any pronounced extent.

EXPERIMENTAL.

2-p-Diethylaminostyrylpyridine-methiodide.—*p*-Diethylaminobenzaldehyde (1.15 g.), α -picoline methiodide (1.53 g.) and piperidine (0.5 c.c.) were dissolved in absolute alcohol (30 c.c.) and the solution boiled under reflux by a rose burner. Within a few minutes, the solution became deep orange and red crystals began to separate out. After 1 hour's heating the solution was cooled, and the crystals recrystallised from methyl alcohol, yield 2.03 g. (80%). (Found: N, 7.25; I, 32.32. $C_{18}H_{23}N_2I$ requires N, 7.11; I, 32.24 per cent).

2-p-Diethylaminostyrylpyridine-ethiodide— α -Picoline ethiodide (3.75 g.), piperidine (1.0 c.c.) and absolute alcohol (70 c.c.) were refluxed

together for 16 hours. After prolonged cooling in a frigidaire (48 hours) crystals separated out which were recrystallised from *n*-propyl alcohol. On concentrating the mother-liquor and again cooling in the frigidaire some more crystals were obtained, yield 4.57 g. (75%). (Found : N, 6.89 ; I, 31.43. $C_{18}H_{26}N_2I$ requires N, 6.86 ; I, 31.13 per cent).

2-p-Diethylaminostyrylpyridine-n-propyl iodide.—A solution of α -picoline-*n*-propyl iodide (3.65 g.), *p*-diethylaminobenzaldehyde (2.45 g.) and piperidine (10 c.c.) in absolute alcohol (60 c.c.) were briskly boiled under reflux ; a deep red colour developed almost immediately and after 3 hours, beautiful shining red crystals were deposited. These were recrystallised from absolute alcohol, yield 5.85 g. (67%). (Found : N, 6.85 ; I, 30.29. $C_{20}H_{27}N_2I$ requires N, 6.64 ; I, 30.09 per cent).

2-p-Diethylaminostyrylpyridine-n-butyl iodide was obtained by refluxing a mixture of α -picoline-*n*-butyl iodide (4.04 g.), *p*-diethylaminobenzaldehyde (2.58 g.), piperidine (1 c.c.) and absolute alcohol (60 c.c.) for 3 hours. A second crop was obtained by distilling off a portion of the alcohol and cooling the mixture. The crystals deposited were recrystallised from absolute alcohol, yield 6.4 g. (76%). (Found : N, 6.58 ; I, 29.4. $C_{21}H_{29}N_2I$ requires N, 6.42 ; I, 29.1 per cent).

The authors are indebted to Professor L. M. Chatterjee of the Physics Department for help in taking the sensitisation spectra. Acknowledgment is made by one of us (D.P.) for the grant of a research scholarship by the Government of Bihar.

THE ALKALOID OF *BERBERIS UMBELLATA*, WALL. PART III.

BY R. CHATTERJEE.

Umbellatine $C_{21}H_{21}O_5N$, the common alkaloid of the Himalyan species of *Berberis* yields on potassium permanganate oxidation hemipinic acid and on potassium hydroxide fusion, protocatechuic acid. These results show that the two methoxy groups, are in adjacent positions in a benzene nucleus in umbellatine and that other groups, like the methylenedioxy and hydroxyl, are not present in the benzene ring containing the two methoxyl groups.

Umbellatine, $C_{21}H_{21}O_5N$, which is found to be present not only in *B. umbellata* (*J. Indian Chem. Soc.*, 1940, **17**, 289; 1942, **19**, 233) but also in other Himalyan species of *Berberis*, e.g., *B. insignis* (*J. Amer. Pharm. Assoc.*, 1941, **30**, 247), *B. lycium*, *B. nepalensis* and *B. Wellichiana* (*Science & Culture*, 1942, **7**, 619) yields hemipinic acid ($C_{10}H_{10}O_6$) on oxidation by potassium permanganate solution, like berberine $C_{20}H_{19}O_5N$, (Perkin, *J. Chem. Soc.*, 1889, **55**, 63) the common alkaloid of the European species of *Berberis*, or other isoquinoline alkaloids, corydaline, $C_{22}H_{27}O_4N$, (Dobbie and Lauder, *J. Chem. Soc.*, 1902, **81**, 145; 1903, **83**, 605), and narcotine, $C_{22}H_{23}O_7N$ (Wöhler, *Annalen*, **50**, 17). Hemipinic acid, thus obtained, melts at $177-78.5^\circ$, which does not eliminate its possibility of being *m*-hemipinic acid, m.p., 175° as obtained from papavarine, $C_{20}H_{21}O_4N$ (Goldschmidt, *Monatsh*, 1888, **9**, 327; *ibid.*, 1888, **9**, 778), and also from corydaline (*loc. cit.*). To elucidate its nature the ethylimide of the hemipinic acid is prepared and its melting point determined as 92° , which proves conclusively the nature of the hemipinic acid as 3 : 4-dimethoxyphthalic acid since the ethylimide of *m*-hemipinic acid melts at $226-27^\circ$.

The production of hemipinic acid shows conclusively that the two methoxy groups present in umbellatine are placed adjacent to each other and that they are present in a benzene ring in the umbellatine molecule. The two carboxyl groups next to the methoxy groups are in all probability produced by the fission of the linkings of a fused ring of the molecule, as in the case of the molecules of other bases, like berberine etc.

Like berberine, umbellatine also yields protocatechuic acid on fusion with solid potassium hydroxide above 250° . Protocatechuic acid might have been obtained by the production and subsequent demethylation and elimination of a molecule of carbon dioxide of one of the two carboxyl

groups of hemipinic acid, since Perkin (*loc. cit.*) has shown that hemipinic acid yields on potash fusion protocatechuic acid.

EXPERIMENTAL.

Permanganate Oxidation of Umbellatine.—Umbellatine hydrochloride (5 g.) was dissolved in warm water (150 c.c.), and treated with potassium carbonate (1.0 g.) solution and then oxidised by slowly running in a solution of potassium permanganate solution (25 g. in 500 c.c. of water). The decolourisation of the permanganate was very rapid at start, and as soon as about 330 c.c. of the solution were added, decolourisation slowed down appreciably, and continued warming was necessary to remove the last traces of the pink colour of the permanganate solution.

The solution was left overnight and then saturated with carbon dioxide gas and filtered from the manganese precipitate. The filtrate and the washings were evaporated completely to dryness on a water-bath, and the residue was soxhletted with absolute alcohol. The residue obtained after removal of the last traces of alcohol, was dissolved in water and the brown aqueous solution was treated with dilute sulphuric acid when a small quantity of sticky matter separated which could not be solidified. The sticky matter was removed by filtration and the filtrate was extracted continuously with ether (100 c.c. in 4 instalments) by shaking each time in a mechanical shaker for 8 hours. The ethereal solution on removal of ether yielded a pale yellow oily residue which solidified when kept in a vacuum desiccator over concentrated sulphuric acid for a week. It was then sublimed at 0.1 mm. pressure when a minute quantity of a yellow liquid separated first at 140-150°, and then a transparent crystalline solid, moist with the liquid, at 150-160°. The moist solid when dried on a porous plate melted at 125°-157°.

The moist solid was well washed with small quantities of ether, dried and powdered and warmed with concentrated hydrochloric acid and kept overnight and filtered from the acid solution and repeatedly washed with cold water in small amount. The filtrate and the washings yielded a very small quantity of a semi-solid which could not be successfully handled. The residue was then dried, m.p. 155°-60°. The melting point further rose to 177-178.5°, on slow crystallisation of the solid from boiling water. (Found in the sample dried in *vacuo* over P_2O_5 at 100°: C, 52.96; H, 4.75. Calc. for $C_{10}H_{10}O_8$: C, 53.1; H, 4.43 per cent). To identify the hemipinic acid thus obtained, the m.p. of the sample was compared with that of hemipinic acid prepared from opianic acid. The hemipinic acid, as

obtained from narcotine melted at 179-80°, and when mixed with that obtained from umbellatine melted at 179°.

The *ethylimide* derivative of hemipinic acid was prepared according to Liebermann (*Ber.*, 1886, 19, 2275), by dissolving the purified acid obtained from umbellatine in an aqueous solution of ethylamine (30%) and evaporating it to dryness. The residue, thus obtained, was heated carefully over a naked flame, and then exhausted with boiling methyl alcohol. On cooling, the ethylimide separated as needles, m.p. 90°. The melting point did not change even on high vacuum sublimation of the ethylimide at 125-135° under 0.15 mm. pressure. The ethylimide of hemipinic acid, obtained from narcotine, was purified by the author by high vacuum sublimation and by repeated crystallisation from water, and was found to melt sharply at 92° (mixed m.p. with the ethylimide of the hemipinic acid from umbellatine). This shows that the hemipinic acid thus obtained is 3 : 4-dimethoxyphthalic acid. (Found in the vacuum dried sample : N, 5.63. Calc. for $C_{10}H_8O_4N$: N, 5.9 per cent).

Fusion of Umbellatine with Potassium Hydroxide.—Umbellatine (1 g.) and potassium hydroxide (6 g.) were heated rapidly with constant stirring in a nickel crucible on a metal-bath. When the temperature reached 270-280°, bubbles of a pungent smelling gas resembling methyl or ethylamine were evolved. The foaming mass was stirred and kept at the above temperature for 10 minutes. The mass was then cooled down quickly to room temperature, and treated with water (30 c.c.) and the dark aqueous solution was saturated with solid ammonium chloride and filtered. On treatment with animal charcoal a clear dark brown coloured filtrate was obtained. The filtrate was extracted with ether, the ethereal solution was washed twice with water and then dried over anhydrous sodium sulphate. On removal of ether, a brown syrupy residue was obtained, which crystallised immediately as needles contaminated with resinous matter. The needles could not be freed from the associated impurities by crystallisation. The aqueous solution of the needles was acidic, and produced a deep emerald green colouration with ferric chloride solution. On adding a solution of sodium carbonate the green colour changed first to blue, then violet and finally red. Like protocatechuic acid, it reduced an ammoniacal solution of silver nitrate and gave with lead acetate solution a white precipitate soluble in acetic acid.

The needles were then purified by high vacuum sublimation at 0.1 mm. pressure. Two fractions were obtained—the one as a slightly brownish coloured crystalline solid at 140-160°, and the other which was the main fraction as colourless crystals, at 160-170°. The first fraction

melted at 103° . The fraction did not depress the m.p. of pyrocatechol and in fact responded to the reactions of pyrocatechol.

The second fraction, the colourless crystals, melted with decomposition at $196-98^{\circ}$, the m.p. of protocatechuic acid. When mixed with an authentic sample of protocatechuic acid the m.p. did not change. (Found: C, 50.1; H, 4.8. Calc. for $C_7H_6O_4$, H_2O : C, 49.0; H, 4.7 per cent).

The author expresses his gratitude to Mr. N. Ghosh, M.Sc. for all the micro-analyses recorded in this paper.

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AURICULARINE—A NEW ALKALOID FROM THE ROOTS AND STEMS OF *HEDYOTIS AURICULARIA*.

By A. N. RATNAGIRISWARAN AND K. VENKATACHALAM.

Chemical examination of the root and stem of *Hedyotis auricularia* has shown the presence of the following constituents: fatty matter yielding on saponification stearic and linoleic acids, a phytosterol, alizarin, oxalic acid, glucose, a crystalline alkaloid, auricularine ($C_{42}H_{55}ON_5$ m.p. 210°) and amorphous bases. Results of micro-analyses show that auricularine is different from the alkaloid hedyotine, isolated from the same plant. Unlike hedyotine, auricularine is a crystalline alkaloid with definite chemical characteristics.

The root of *Hedyotis auricularia* was examined by Dey and Lakshminarayanan (*Arch. Pharm.*, 1933, 271, 485) and was found to contain, besides a fatty oil, glucosides, reducing sugars, colouring matter, tannins and albumins and an alkaloid named 'Hedyotine' ($C_{18}H_{22}O_5N_2$). The alkaloidal base could not, however, be obtained by them in a stable form, as they found it to change rapidly into a pasty mass on exposure to air. The hydrochloride and the nitrate of the alkaloid were, on the other hand, reported very stable and could be obtained in crystalline condition.

A fresh chemical investigation of the plant was undertaken in this laboratory in order to isolate, if possible, hedyotine base in crystalline condition, and to find out if any other constituents were present to which the ascribed amoebicidal action of the drug could be attributed. As a result a stable, crystalline alkaloid has been isolated, though in very poor yield. But it appears to be different from hedyotine, because the results of micro-combustion show that its formula is $C_{42}H_{55}ON_5$, while hedyotine is stated to have a simpler formula, and further, it does not yield the coloured crystalline salts described by the previous workers (*loc. cit.*). The melting point of the picrate of the new crystalline alkaloid (217-18° decomp.) is also widely different from that of hedyotine picrate which is stated to melt at 265° with decomposition. It is, therefore, apparent that the crystalline alkaloid, now isolated, is different from hedyotine, and the name *Auricularine* is proposed for it. As the yield of the alkaloid is only about 0.001% of the dried plant, a sufficient quantity could not be isolated for a detailed examination.

The uncrystallisable residues left after the separation of auricularine still contained a large amount of alkaloidal matter from which no crystalline base, but only a microcrystalline hydriodide (m.p. 215-20° decomp.) could

be isolated. Further attempts to obtain crystalline material from this fraction are in progress.

The other constituents found to be present in the alcoholic extract of the drug are : fatty matter, yielding on saponification stearic and linoleic acids, a phytosterol, (m.p. 141-42°), alizarin, uncrystallisable substances which give colour reactions similar to those of oxymethylanthraquinone compounds, oxalic acid and glucose.

EXPERIMENTAL.

The material for the investigation consisting of the stem and root of the plant was supplied to us by the Forest Department of the Travancore State to whom we are deeply indebted.

Examination for alkaloid by extraction with Prolious's fluid gave marked reactions with the usual reagents.

The powdered plant was assayed for alkaloidal content by a gravimetric method based on the U.S.P. IX method for assay of Belladonna root, using as solvent a mixture of three volumes of ether and one volume of chloroform. The alkaloidal content of the plant was, on an average, 0.29% of the dried material.

Isolation of Auricularine.—25 Kg. of the powdered drug were extracted with 90% alcohol and the solvent was distilled off under reduced pressure. The residue (568 g.) was treated with benzene in order to remove fats and waxes, and the benzene extract (A) was reserved for further examination.

The residue that remained insoluble in benzene was repeatedly shaken with 2% sulphuric acid solution till the acid extract ceased to give alkaloidal reactions. The benzene extract (A) was also extracted with dilute sulphuric acid solution to recover any dissolved alkaloid, and the combined acid solution was shaken with ether to remove non-basic impurities. The aqueous acid solution was then nearly neutralised with 5% sodium carbonate solution, taking care that the solution remained distinctly acidic to litmus. The precipitated impurities were filtered off, excess of strong ammonia was added to the filtrate, and the solution was shaken with chloroform till no more alkaloid was extracted with the chloroform. The chloroform solution was washed with distilled water and dried with anhydrous sodium sulphate. On evaporating off the chloroform, a brownish residue was left (14.6 g.) which was dissolved in 10% acetic acid solution. To this solution was then added a strong solution of potassium nitrate till no further precipitation occurred. The precipitate was filtered off after standing overnight, and the filtrate was rendered alkaline by the addition of ammonia. The precipitated alkaloid was filtered under suction, washed thoroughly with

distilled water, and dried in a vacuum desiccator. The dried alkaloid was then extracted with benzene in a Soxhlet and the benzene solution was decolourised with animal charcoal and filtered. The residue from the benzene extract was dissolved in alcohol and the solution neutralised with 5% alcoholic solution of oxalic acid. On adding a little water and leaving it in the refrigerator for a day, thin glistening needles of auricularine oxalate separated out, which were rapidly filtered under suction and washed with 95% alcohol. The oxalate was recrystallised from 70% alcohol. On heating, auricularine oxalate turned brown at 185° and charred at 230° without melting.

The oxalate was dissolved in water, excess of ammonia was added to the solution, and the precipitated alkaloid was shaken with ether. The ethereal solution was shaken with water and dried with anhydrous sodium sulphate. On spontaneous evaporation of the ether, auricularine was obtained in the form of colourless rosettes of needles, yield 0.2 g. It was recrystallised from 90% alcohol. On heating, auricularine turned brown at 192° and melted with decomposition at 201° .

On drying in *vacuo* over phosphorus pentoxide at 100° , the crystals suffered a loss of weight of 2.65%. $C_{42}H_{55}ON_5, H_2O$ requires a loss of weight of 2.71%. (Found in the dried sample: C, 78.24; H, 8.64; N, 10.62. $C_{42}H_{55}ON_5$ requires C, 78.07; H, 8.59; N, 10.85 per cent).

Auricularine picrate was obtained as a microcrystalline yellow powder by mixing an alcoholic solution of auricularine with an alcoholic solution of picric acid and recrystallising from alcohol. On heating, the picrate melted with decomposition and frothing at $217-18^{\circ}$.

The mother-liquors after the crystallisation of auricularine oxalate were diluted with water, made alkaline with strong ammonia, and shaken with ether. The ethereal solution was washed with water and dried with anhydrous sodium sulphate. The residue left after evaporating off the ether was dissolved in dilute acetic acid and mixed with a slight excess of a concentrated solution of potassium iodide. A cream coloured microcrystalline precipitate was obtained, which was washed with a dilute solution of potassium iodide and dried in a vacuum desiccator over sulphuric acid, yield 1.4 g. On heating, the hydriodide turned dark in colour at 195° and charred without melting at $215-20^{\circ}$. Attempts to obtain a crystalline base from the salt have not yet been successful.

Isolation of Alizarin.—The benzene extract (A) from above was treated with sodium hydroxide solution till the latter was no longer coloured violet. The addition of baryta water to the solution caused a purplish precipitate which was well washed with water to remove soluble barium compounds

The washed precipitate was then suspended in boiling water and mixed with hydrochloric acid when an orange coloured precipitate separated. This was filtered; washed and dried. On crystallising from benzene, reddish needles, m.p. 279° , were obtained which gave all the reactions characteristic of alizarin. The filtrate from the baryta precipitation did not yield any crystalline substance.

Fatty Constituents.—The residue from the benzene extract (A) after the alizarin had been separated was examined for fatty acids and non-saponifiable constituents by the usual methods.

Non-saponifiable Constituents.—A crystalline phytosterol, m.p. $141-42^{\circ}$, yielding a crystalline acetate, m.p. $128-29^{\circ}$, was isolated from this fraction.

Saturated Fatty Acids.—An acid, m.p. 67° and having a molecular weight of 342 was obtained which would appear to be stearic acid.

Unsaturated Fatty Acids.—The presence of linoleic acid was indicated in this fraction by the fact that on oxidation with alkaline potassium permanganate solution a tetrahydroxystearic acid, m.p. $154-55^{\circ}$, could be obtained.

Other Constituents.—The alkaline aqueous solution remaining after the separation of the alkaloids was neutralised with acetic acid and treated with a slight excess of neutral lead acetate solution. The precipitate obtained was washed and submitted to the method of separation of organic acids (Fleischer, *Arch. Pharm.*, 1874, 205, 97). The presence of oxalic acid was indicated by its typical reactions in the portion of the lead precipitate insoluble in ammonia.

The filtrate from the lead precipitate was treated with hydrogen sulphide, lead sulphide was filtered off, and the filtrate was concentrated under vacuum. The syrupy residue gave the usual reactions of a reducing sugar, and yielded an osazone, m.p. 105° , indicating the presence of glucose

FORMYLATION OF METHYL γ -RESORCYLATE BY GATTERMANN REACTION: SYNTHESIS OF METHYL 2:6-DIHYDROXY-3-FORMYLBENZOATE.

BY (MISS) K. S. RADHA AND R. C. SHAH.

Methyl γ -resorcyate has been subjected to Gattermann reaction giving methyl 2:6-dihydroxy-3-formylbenzoate, several derivatives of which are studied and the constitution of the ester is established.

Although phenols undergo the usual Gattermann reaction readily, phenolic esters cannot be readily formylated due, no doubt, to the deactivating effect of the carbomethoxy group. Thus methyl β -resorcyate does not undergo the usual Gattermann reaction, but it can only be formylated by Shah and Laiwalla's modified Gattermann reaction using anhydrous aluminium chloride in dry ether (Shah and Laiwalla, *J. Chem. Soc.*, 1938, 1828).

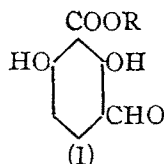
Methyl γ -resorcyate has now been studied for comparison and it has been found that the formylation proceeds under the usual condition, in absence of anhydrous aluminium chloride. The product obtained has been proved to have the structure of methyl 2:6-dihydroxy-3-formylbenzoate (I, R=Me) and has been characterised by the preparation of its 4-nitrophenylhydrazone and semicarbazone derivatives.

The present study thus shows that the carbomethoxy group in the γ -position has no deactivating effect on the reactivity of the resorcinol nucleus, whereas the carbomethoxy group in the β -position has considerable deactivating effect. This is analogous to the difference in the reactivity between the 2-acetyl and 4-acetylresorcinols, the former of which is almost as reactive as resorcinol as regards Pechmann's condensation with ethyl acetoacetate, while the latter is much less reactive. On hydrolysis it affords the corresponding acid (I, R=H), which on decarboxylation gives β -resorcyaldehyde, which establishes the structure of the formyl ester.

The *ortho*-hydroxy-aldehyde structure has been further proved by the formation of coumarin derivatives namely, methyl 7-hydroxy-3-acetylcoumarin-8-carboxylate and ethyl 7-hydroxy-8-carbomethoxycoumarin-3-carboxylate with ethyl acetoacetate and ethyl malonate respectively by the Knoevenagel reaction.

On Clemmensen reduction the formyl ester yields methyl 2:6-dihydroxy-3-methylbenzoate, bromination and nitration of which yields

methyl 2,6-dihydroxy-3-formyl-5-bromobenzoate and methyl 2,6-dihydroxy-3-formyl-5-nitrobenzoate respectively.



E X P E R I M E N T A L.

Methyl 2:6-Dihydroxy-3-formylbenzoate (I, R=Me).—To a solution of anhydrous methyl γ -resorcyate (3 g., 1 mol.) in dry ether in a flask, cooled by freezing mixture, zinc cyanide (4.2 g., 2 mols.) was added followed by a further addition of dry ether (50 c.c.). Dry hydrogen chloride was then passed for 5 to 6 hours through the cooled solution which was kept well stirred all the time. The zinc cyanide gradually disappeared, the solution turned pinkish and a pasty mass separated.

The ether was decanted and water (50 c.c.) was added to the pasty mass and the mixture was heated on a water-bath for about 2 hours and the mixture filtered hot. The filtrate deposited very long golden yellow needles on cooling, which on crystallisation from glacial acetic acid gave colourless needles, m.p. 113-115°. (Found: C, 55.3; H, 4.6. $C_9H_8O_5$ requires C, 55.1; H, 4.1 per cent).

The experiment was repeated with the addition of anhydrous aluminium chloride in dry ether, when the reaction mixture turned reddish brown and no product could be isolated nor the original γ -ester recovered.

The 2:4-dinitrophenylhydrazone, prepared as usual, was crystallised from glacial acetic acid in tiny orange needles, m.p. 272-75° (decomp.). (Found: N, 14.9. $C_{16}H_{12}O_8N_4$ requires N, 14.9 per cent).

The semicarbazone, prepared as usual, was crystallised from hot alcohol in small needles, m.p. 220-22°. (Found: N, 16.2. $C_{10}H_{11}O_5N_3$ requires N, 16.6 per cent).

Methyl 7-Hydroxy-3-acetylcoumarin-8-carboxylate.—Piperidine (4 drops) was added to a mixture of the formyl ester (1 g.) and ethyl acetoacetate (1 g.) dissolved in pyridine (10 c.c.) and the mixture was heated at 100° on a water-bath for 1 hour. The solid, obtained on acidifying with dilute hydrochloric acid, crystallised from hot alcohol in greyish white needles, m.p. 245-46°. (Found: C, 59.4; H, 4.8. $C_{13}H_{10}O_6$ requires C, 59.5; H, 4.8 per cent).

Ethyl 7-Hydroxy-8-carbomethoxycoumarin-3-carboxylate.—The formyl ester (1 g.) was condensed with ethyl malonate (1 g.) in the presence of piperidine (4 drops) by heating on a water-bath for 2 hours. The product

obtained on acidification was crystallised from hot alcohol in tiny colourless needles, m.p. 255-56°. (Found: C, 57.0; H, 4.0. $C_{14}H_{12}O_7$ requires C, 57.5; H, 4.1 per cent).

Methyl 2:6-Dihydroxy-3-methylbenzoate.—The formyl ester (1 g.), dissolved in hot alcohol (10 c.c.), was gradually added to a mixture of zinc amalgam, prepared from zinc dust (5 g.) according to Robinson and Shah, (*J. Chem. Soc.*, 1934, 1497) and dilute hydrochloric acid (1:1, 25 c.c.) at 100°. More alcohol was added whenever necessary to keep the ester in solution. After one hour concentrated hydrochloric acid (5 c.c.) was added and heating continued for further $\frac{1}{2}$ hour. The reaction mixture was extracted with ether. On cooling, the extract left an oil which on being kept in the frigidaire for several days deposited very fine long pink needles, m.p. 62-63°. (Found: C, 64.8; H, 5.6. $C_9H_{10}O_3$ requires C, 65.1; H, 6.0 per cent).

2:6-Dihydroxy-3-formylbenzoic Acid (I, R=H).—The formyl ester (0.3 g.) was heated on a boiling water-bath for 2 hours with sodium hydroxide (10 c.c., 10%). The solution was acidified and extracted with ether. The yellow solid left on evaporation of the ether was crystallised from hot water in small pale yellow needles, m.p. 215-16°. (Found: C, 52.3; H, 3.8. $C_8H_6O_5$ requires C, 52.7; H, 3.3 per cent).

Decarboxylation of the acid was carried out by heating the acid (0.3 g.) in a Carius tube with water (10 c.c.) and hydrochloric acid (1:1, 1 c.c.) for 8-9 hours at 180-190° when a solid was obtained. This was washed with sodium bicarbonate solution and crystallised from hot alcohol in very pale yellow needles, m.p. 132-34°. Mixed melting point with an authentic specimen of β -resorcyaldehyde was not depressed.

Methyl 2:6-Dihydroxy-3-formyl-5-nitrobenzoate.—The formyl ester (0.5 g.) was dissolved in concentrated sulphuric acid (5 c.c.) and concentrated nitric acid was added with external cooling. The mixture was left overnight and the solid separating was crystallised from hot alcohol in long pale yellow needles, m.p. 148-50°. (Found: N, 5.6. $C_9H_7O_7N$ requires N, 5.8 per cent).

Methyl 2:6-Dihydroxy-3-formyl-5-bromobenzoate.—The formyl ester (1 g.) was dissolved in glacial acetic acid. Bromine (0.5 c.c.) in glacial acetic acid (10 c.c.) was added with stirring. The product obtained on diluting the solution the next day was crystallised from dilute alcohol, m.p. 143-45°. (Found: Br, 28.9. $C_9H_7O_5Br$ requires Br, 29.0 per cent).

ORGANIC ANALYTICAL REAGENTS CONTAINING SULPHUR.

BY ANIL KUMAR MAJUMDAR.

Dimercaptothiobiazole (Losanitsch, *J. Chem. Soc.*, 1922, **121**, 2544) and phenyldithiobiazolonthiol (Busch, *Ber.*, 1894, **27**, 2511) having the reacting groups RN-CS-S-C(SH)=N , have been found to give coloured precipitates with the metals of the sulphide group.

The reagent dimercaptothiobiazole gives red precipitate with bismuth, white to yellow precipitate with other metals of the sulphide group, excepting mercury with which it gives a black precipitate, while the reagent phenyldithiobiazolonthiol gives yellow precipitates with gold, mercury, lead, silver, platinum, arsenic and antimony, white with cadmium and zinc, brown with copper, brick-red with tin and red precipitates with bismuth and palladium.

Dubsky and co-workers (*Z. anal. Chem.*, 1934, **96**, 267, 412) have used both the reagents for the detection of very small quantities of bismuth, their identification limit being 1.2 $\mu\text{g.}$ and sensitivity 1 part in 28,000 parts.

Ray and Gupta (*J. Indian Chem. Soc.*, 1935, **12**, 308) found with the reagent dimercaptothiobiazole that the identification limit reaches 0.1 $\mu\text{g.}$ and sensitivity one part in 1,600,000 parts if nitric and not hydrochloric acid solution of bismuth is used.

Recently it has been observed by the author that the red precipitates of the bismuth compounds given by both the reagents can be peptised by a solution of gum acacia of suitable concentration and that the colours developed can be used for the estimations of bismuth, as the intensity of colours varies regularly according to Beer's law.

Also it has been observed that the colouration limit with both the reagents reaches one part in 6,000,000 parts if a very dilute nitric acid solution of bismuth is used and that bismuth up to the extent of 37 in 20 c.c. solution can be estimated with a high degree of accuracy.

The details of the methods for the colorimetric estimations of bismuth as well as other possible uses of the reagents will be published shortly.

MIXED CATION EFFECTS IN THE ESTIMATION OF BASE-EXCHANGE CAPACITIES OF HYDROGEN CLAYS.*

BY J. N. MUKHERJEE, R. P. MITRA AND K. C. GHOSH.

In a number of previous publications (Mitra, *Indian J. Agric. Sci.*, 1936, 6, 555 ; J. N. Mukherjee, Mitra and S. Mukherjee, *Trans. Nat. Inst. Sci. India*, 1937, 1, No. 10, 227 ; Mitra, S. Mukherjee and Bagchi, *Indian J. Agric. Sci.*, 1940, 10, 303 ; Mitra, *ibid.* p. 317 ; Mitra and Mitra, *ibid.*, p. 344 ; Mitra, *Bull. Indian Soc. Soil Sci.*, 1942, No. 4, 41) it has been shown that the base exchange capacity (B.E.C.) of a hydrogen clay is not a fixed quantity but depends on the p_H at which it is estimated and on the nature and concentration of cations introduced into the system in making the estimation. At a fixed p_H , e.g., p_H 7.0, the B.E.C. calculated from titration curves with different bases decreases in the order $\text{Ca(OH)}_2 > \text{Ba(OH)}_2 > \text{NaOH}$. When, however, the titration is carried out in the presence of a fixed concentration of the corresponding salts having a common anion, e.g., chlorides, the B.E.C. follows the order : $\text{BaCl}_2, \text{Ba(OH)}_2 > \text{CaCl}_2, \text{Ca(OH)}_2 > \text{NaCl}, \text{NaOH}$. The greater relative effect of Ca^{++} compared with Ba^{++} in the absence of salts constitutes an *irregular* or *specific* cation effect in the sense that the lyotrope series is not followed. In the presence of salts, the cation effect is *regular*. It has been found that the greater part of the reaction with the base takes place at a lower p_H when salts are present than when the bases alone are used. In the papers cited above these two types of cation effect have been reconciled in the light of the theory of the electrical double layer and of adsorption of ions assuming that in the presence of salts cations are adsorbed in a hydrated condition and when salts are absent, adsorption of more or less dehydrated cations takes place.

Other peculiarities of the cation effect, not clearly recognised by previous workers, have also been recorded and are discussed below. They were observed when the added salt had cations *other than those of the base* used for the titration. A clear understanding of such *mixed cation effects* is desirable as the soil absorption complex usually contains more than one

* This work has been carried out under a scheme of research financed by the Imperial Council of Agricultural Research, India.

type of exchangeable cations and the part they may play, individually and relatively to each other, on the base exchange and other reactions of the complex is not definitely known. Some results obtained with a hydrogen clay from a black cotton soil from Padegaon are given in Table I. As B.E.C.'s at a fixed p_H , viz., p_H 7.0 have been compared, their variations arise only out of the peculiarities of the cation effect.

TABLE I.

Base exchange capacity.

At p_H 7.0 in m.e. base per 100 g. H. clay with

| System. | NaOH. | Ba(OH) ₂ . | Ca(OH) ₂ |
|-----------------------------|-------|-----------------------|---------------------|
| Sol+0.002N-NaCl | 63.0 | 67.0 | 67.0 |
| „ +0.002N-BaCl ₂ | 68.0 | 70.0 | 70.0 |
| „ +0.002N-CaCl ₂ | 67.0 | 70.0 | 69.0 |
| „ +0.1N-NaCl | 80.0 | 87.0 | 85.0 |
| „ +0.1N-BaCl ₂ | 114.0 | 122.0 | 119.0 |
| „ +0.1N-CaCl ₂ | 110.0 | 120.0 | 116.5 |

The B.E.C. with a given base in the presence of a fixed concentration of different salts follows the order : $\text{BaCl}_2 > \text{CaCl}_2 > \text{NaCl}$ in agreement with the regular cation effect. The same order : $\text{Ba}^{++} > \text{Ca}^{++} > \text{Na}^+$ of the relative effects of the cations is also observed when different bases are used in conjunction with any one of the above salts ; the B.E.C. follows the order : $\text{Ba(OH)}_2 > \text{Ca(OH)}_2 > \text{NaOH}$. It is interesting to note, however, that in the presence of either BaCl_2 or CaCl_2 , NaOH gives a smaller B.E.C. than Ba(OH)_2 or Ca(OH)_2 , although the concentration of the divalent cations cannot be materially different in the titration with the three bases. Some sort of an *ionic antagonism* between the comparatively few Na^+ ions on the one hand and the large number of Ba^{++} and Ca^{++} ions on the other, is indicated. The otherwise greater effect of the divalent cations and their capacity to displace acid from the colloidal particles appear to be somewhat inhibited by the Na^+ ions present at a much lower concentration.

EFFECT OF NON-ELECTROLYTES ON THE p_H AND SPECIFIC CONDUCTIVITY OF HYDROGEN CLAY SOLS.*

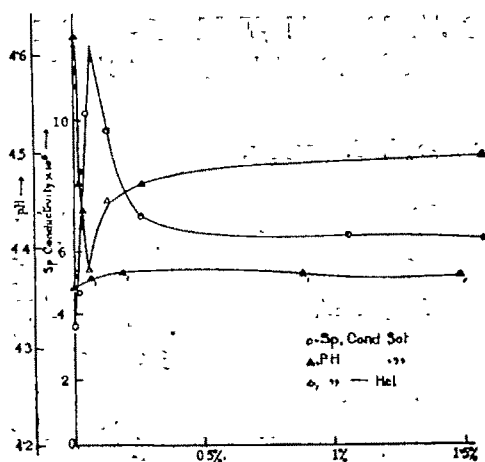
By R. P. MITRA AND K. C. GHOSH.

Hydrogen clay, as usually obtained from the clay fraction of soil by electrodialysis or repeated leaching with a dilute mineral acid after treatment with 6% hydrogen peroxide to oxidise organic materials contained in it, has characteristic acidic properties (Mitra, *Indian J. Agric. Sci.*, 1936, **6**, 555; 1940, **10**, 317 *et seq*). The pre-treatment with 6% hydrogen peroxide may not effect a complete removal of the organic matter in all cases. If a hydrogen clay containing some residual organic matter (r.o.m.) is treated with an organic solvent a part of the r.o.m. may be dissolved. Some peculiar observations have been made by us in this connection. It has been found that the addition of traces of alcohol to a hydrogen clay sol produces a sharp rise in the specific conductivity and a correspondingly sharp fall in the p_H (*cf.* Fig. 1). As the concentration of alcohol increases, the conductivity reaches a maximum value and then rapidly decreases and finally tends to remain constant; at the same time, the p_H passes through a minimum value and then increases approaching a constant value towards the end. The maximum conductivity and the minimum p_H are observed at about the same concentration of the added alcohol. On the other hand, control experiments with a hydrochloric acid solution having nearly the same p_H as the sol show that alcohol has practically no effect on the p_H and specific conductivity of the former within the range of concentration (0 to 1.5%) of the alcohol used. The above discontinuous variations in the p_H and specific conductivity of the sol, especially the maximum and minimum, are interesting though it is at present difficult to visualise their real significance. They do not appear to have been previously observed.

The p_H and conductivity of the sol-alcohol mixture change with time. The conductivity tends to increase while the p_H slowly decreases. A slow reaction between the sol and the alcohol is indicated. The curves

* The work has been carried out under a scheme of research financed by the Imperial Council of Agricultural Research, India, and directed by Prof. J. N. Mukherjee.

shown below were obtained from measurements made 72 hours after the addition of alcohol to the sol.



The decrease in the conductivity and H^+ -ion concentration of the sol at higher concentrations of the alcohol after an initial increase shows that the alterations in the p_H and conductivity cannot be referred to a simple dissolution of acids from the hydrogen clay by the alcohol, as in that case both the H^+ -ion concentration and the conductivity would go on increasing with increasing concentration of alcohol in the

mixture instead of decreasing at the higher concentrations. A hydrogen clay was repeatedly leached with 25% alcohol. It was then washed free from the alcohol and redispersed in water. The p_H and specific conductivity of the redispersed sol showed similar discontinuous variations as the original sol on the addition of small quantities (0 to 2%) of alcohol.

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FREE AND TITRATABLE ACIDS PER PARTICLE OF SUBFRACTIONS OF HYDROGEN CLAY.*

BY R. P. MITRA AND S. P. RAY.

Subfractions having particle sizes ranging between specified limits have been separated from the entire clay fraction of a black cotton soil by controlled centrifugalisation following Ayre's technique as described by Whitt and Bayer (*J. Amer. Soc. Agron.*, 1937, **29**, 917). Free and titratable acids of 0.25% suspensions of hydrogen clays prepared from them have been calculated respectively from the E.M.F. of the hydrogen electrode and the inflexion point of potentiometric titration curve with NaOH. If T is the free or titratable acid (in normality) per g. the corresponding quantity *per particle* is $4\pi^3 DT/3$, where $2r$ is the equivalent spherical diameter and D , the density. Also, the *number* of free or titratable H^+ ions per particle is the product of the free or titratable acid per particle and Avogadro's number. The results are given in Table I.

TABLE I.

| Reference number of hydrogen clay. | Equivalent spherical diameter in microns | Free acid (normality) per particle $\times 10^{21}$. | Titratable acid (in normality) per particle $\times 10^{21}$. | Number of free H^+ ions per particle | Number of titratable H^+ ions per particle. |
|------------------------------------|--|---|--|--|---|
| Padegaon-B -1 | 1.1 | 8.1×10^5 | 8.4×10^5 | 4.9×10^8 | 5.0×10^8 |
| " -2 | 0.15 | 5.4×10^3 | 2.7×10^3 | 3.2×10^4 | 1.6×10^5 |
| " -3 | 0.07 | 8.7×10^2 | 2.9×10^2 | 3.7×10^3 | 1.7×10^5 |
| " -4 | 0.03 | 8.6×10 | 2.3×10 | 5.2×10^2 | 1.4×10^4 |
| " -5 | 0.018 | 9.4 | 5.1 | 5.7×10 | 3.0×10^3 |

The number of free H^+ ions associated with the largest particles is of the order of 10^8 and that of titratable H^+ ions of the order of 10^8 . Both decrease rapidly with diminishing particle size. However, each particle of the finest subfraction has as many as 3×10^3 titratable H^+ ions. The titration curve of this as well as the other subfractions, however, reveals

* The work has been carried out under a scheme of research financed by the Imperial Council of Agricultural Research, India, and directed by Prof. J. N. Mukherjee.

only a monobasic acid character. Other peculiarities of the titration curves have been discussed elsewhere (Mitra, *Indian J. Agric. Sci.*, 1936, 6, 555 ; 1940, 10, 317 ; Mitra, *Bull. Indian Soc. Soil. Sci.*, 1942, No. 4, 41 ; Mukherjee, Mitra and Mukherjee, *Trans. Nat. Inst. Sci. India*, 1937, 1, 227).

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ON THE MODE OF REACTIVITY OF ORCINOL WITH MALIC ACID.

BY V. V. K. SASTRY.

By condensing orcinol with ethyl acetoacetate Pechmann and Cohen (*Ber.*, 1884, 17, 2188) obtained a substance to which they assigned the formula, 7-hydroxy-4:5-dimethylcoumarin, from analogy with the condensation of resorcinol with the same ester. The constitution of this compound was later investigated by Dey (*J. Chem. Soc.*, 1915, 107, 1614) who established it as 5-hydroxy-4:7-dimethylcoumarin from a detailed investigation of the corresponding coumarin-4-acetic acid.

Pechmann and Welsh (*Ber.*, 1884, 17, 1649) condensed orcinol with malic acid in the presence of concentrated sulphuric acid and described the product as 7-hydroxy-5-methylcoumarin. As a result of the above-mentioned work of Dey there has been a tendency to regard this compound also as a 5-hydroxycoumarin derivative (Sen and Chakravarti, *J. Indian Chem. Soc.*, 1929, 6, 793). But the coumarin obtained by them exhibits marked fluorescence when dissolved in aqueous alkali or in concentrated sulphuric acid and in this respect behaves differently from 5-hydroxycoumarins. Ranganadhras (M.Sc. thesis, Andhra University, 1940) has, however, recorded the formation of some quantity of 5-hydroxy-7-methylcoumarin besides the 7-hydroxy-5-methylcoumarin and the coumarino- α -pyrone, by using a higher molecular proportion of malic acid and heating at 100° (*cf* Sen and Chakravarti, *loc. cit.*). It appears, therefore, that orcinol behaves in two different ways in respect of its nuclear reactivity with malic acid. The simultaneous reactivity of both the β and γ positions of orcinol has been observed by Desai and Vakil (*Proc. Indian Acad. Sci.*, 1940, 12A, 391) in the case of the internal Friedel and Crafts' reaction. The synthesis of 5-hydroxy-7-methylcoumarin starting from ethyl haematommate has been described by Sastry and Seshadri (*ibid.*, 1940, 12A, 498) and this compound is very different from the isomer obtained by Pechmann and Welsh and its solutions are deep yellow in colour without fluorescence. Consequently their compound should be 7-hydroxy-5-methylcoumarin whose synthesis starting from orcylic aldehyde has been described by Rao and Seshadri (*ibid.*, 1941, 13A, 253). The author has studied these condensations in greater detail by employing varying molecular proportions of malic acid and heating at different temperatures.

Orcinol and malic acid in equimolecular proportions, were condensed according to the method of Pechmann and Welsh (*loc. cit.*). After adding

sulphuric acid the mixture was heated over a wire gauze using a micro-burner until the reaction was complete.

The product was obtained as pale yellow flat needles and tablets, m.p. 248° . It gave no colour with alcoholic ferric chloride. Its solution in aqueous alkali and concentrated sulphuric acid was colourless exhibiting blue fluorescence. It was found to be identical with 7-hydroxy-5-methylcoumarin (Rao and Seshadri, *loc. cit.*).

The above experiment was repeated using a water-bath kept at $70-80^{\circ}$ for heating the mixture. After heating for 3 hours the product was worked up and found to be 7-hydroxy-5-methylcoumarin. Similar results were obtained on repeating the experiment with two molecular proportions of malic acid.

By condensing orcinol (1 mol.) and malic acid (1.5 mol.) on the water-bath (3 hours) in the presence of concentrated sulphuric acid a yellow product was obtained which left on boiling with an insufficient amount of alcohol, a fairly good quantity of white residue. This residue (A) was exhausted with alcohol to remove the yellow substance (B) associated with it and then recrystallised from pyridine or glacial acetic acid when colourless needles melting at 345° were obtained. This substance is sparingly soluble in ether, chloroform and benzene and moderately soluble in boiling alcohol and acetone. It is insoluble in ammonia, but dissolves in hot caustic alkalis with a yellow colour and is identified as a coumarino- α -pyrone.

The yellow alcoholic solution obtained above was concentrated to a small volume when the substance (B) crystallised out. On further crystallisation pale yellow flat needles and tablets of 7-hydroxy-5-methylcoumarin, melting at 248° , were obtained. The substance does not give a colour reaction with alcoholic ferric chloride. It dissolves in aqueous alkali and concentrated sulphuric acid with blue fluorescence. The same products were obtained even when 2 mols. of malic acid were employed.

These experiments were repeated by heating orcinol at 120° with different proportion (1, 1.5, and 2 mols.) of malic acid and the results were similar to those obtained above excepting that some resinification took place probably due to the high temperature employed.

From these experiments it is, therefore, to be concluded that orcinol reacts with malic acid only in the β -position and consequently no 5-hydroxy-7-methylcoumarin is produced.

LIMITING EXCHANGE OF ALUMINIUM IONS FROM HYDROGEN CLAYS ON THE ADDITION OF NEUTRAL SALTS*

BY J. N. MUKHERJEE, B. CHATTERJEE AND P. C. GOSWAMI.

Different opinions have been expressed regarding the amount of Al^{+++} ions liberated on the addition of neutral salts to hydrogen clays (Mattson, *Soil Sci.*, 1928, **28**, 845; Paver and Marshall, *J. Soc. Chem. Ind.*, 1934, **53**, 750). Estimations are recorded in this note of the amounts of Al displaced from a hydrogen clay sol, Latekujan-F, after each successive leaching with normal solutions of $BaCl_2$ and $CaCl_2$ respectively till no Al in the leachate could be detected with 8-oxyquinoline (Berg, *Z. anal. Chem.*, 1927, **71**, 369). The residue remaining after leaching with $N-BaCl_2$ in the above manner was converted† into hydrogen clay, repeatedly leached with $N-BaCl_2$, as in the previous case and the amounts of Al were estimated in each leachate. The whole sequence of operations described above was repeated nine times. The results are shown in Tables I and II.

TABLE I.

Hydrogen clay taken = 100 c.c. Colloid content = 25.2 g/litre.

N-salt solution used for each leaching operation = 125 c.c.

| Leaching | Barium chloride | | | Calcium chloride | | |
|----------|-----------------|------|-----------------|------------------|------|-----------------|
| | Al displaced‡. | pH. | Total acidity‡. | Al displaced‡. | pH. | Total acidity‡. |
| 1st | 23.2 | 3.32 | 30.0 | 20.8 | 3.22 | 23.2 |
| 2nd | 1.8 | 3.74 | 3.5 | 1.8 | 3.77 | 5.0 |
| 3rd | 0.4 | 3.98 | 1.0 | 0.45 | 3.80 | 2.7 |
| 4th | 0.1 | 4.10 | 0.74 | 0.18 | 4.0 | 0.8 |
| 5th | Nil | 4.54 | 0.26 | Nil | 4.02 | 0.6 |
| Total | 23.4 | ... | 35.5 | 23.23 | ... | 32.3 |

*The results have been taken from the annual report for 1941-42 submitted to the Imperial Council of Agricultural Research, India on the working of the "Scheme of Research into the Properties of Colloid Soil Constituents".

†By treatment with $N/50-HCl$.

‡Results are expressed in m.e. per 100 g. of colloid.

Displaced Al and total acidity both decrease with the progress of leaching till the amount of Al falls below 0.002 mg. per 10 c.c. but that of H^+ ions remains at about $2.8 \times 10^{-5}N$ with $BaCl_2$ and $9.6 \times 10^{-5}N$ with $CaCl_2$. The rapid rate at which the quantity of displaced Al^{+++} falls with progressive leaching indicates that there is a limit to the displacement of Al^{+++} by Ba^{++} under these conditions. The total amount of Al thus obtained does not, however, represent the maximum amount of exchangeable Al (Table II). Ba^{++} ions displace more Al^{+++} and H^+ ions compared to Ca^{++} ions. This is in agreement with the lyotrope series and the *cation effect is regular* (Mukherjee, Mitra and Mukherjee, *Trans. Nat. Inst. Sci. India*, 1937, 1, 227; Chatterjee, *J. Indian Chem. Soc.*, 1939, 16, 589). Comparing results of leaching with $BaCl_2$ with those with $CaCl_2$, somewhat greater amounts of Al are found with $CaCl_2$ in the third to fifth leachates of the two salts and the p_H of the corresponding leachates of $CaCl_2$ is slightly lower. It appears that more displaceable Al^{+++} remains after the first leaching with $CaCl_2$ and hence more Al^{+++} and H^+ come out in later leachings.

TABLE II

No. of leaching of H^+ clay with 125 c.c. $N-BaCl_2$.

| Serial No. of treatment of H-clay with * $BaCl_2$. | M. equiv. of displaced Al in leachate (calc. per 100 g. colloid). | | | | | Total Al displaced (m.e.) per 100 g. |
|--|---|------|------|------|------|---|
| | 1st. | 2nd. | 3rd. | 4th. | 5th. | |
| 1st | 23.20 | 1.80 | 0.40 | 0.10 | Nil | 25.50 |
| 2nd | 8.30 | 0.25 | 0.20 | Nil | " | 8.75 |
| 3rd | 4.62 | 0.33 | Nil | " | " | 4.65 |
| 4th | 4.60 | 0.04 | " | " | " | 4.64 |
| 5th | 4.53 | Nil | " | " | " | 4.53 |
| 6th | 3.20 | " | " | " | " | 3.20 |
| 7th | 3.90 | " | " | " | " | 3.90 |
| 8th | 3.30 | " | " | " | " | 3.30 |
| 9th | 3.40 | " | " | " | " | 3.40 |

* Reconversion of the resulting Ba-clay into H-clay followed by leaching.

The amount of Al displaced by BaCl_2 is considerably reduced after the first treatment but Al^{+++} ions continue to be liberated tending to a constant value of about 3.4 m.e. for the first leachate. Mattson (*loc. cit.*) found that as often a soil was rendered unsaturated by treatment with dilute acid and then treated with neutral salt solutions, Al and Fe are brought into solution. Paver and Marshall (*loc. cit.*), on the other hand, conclude from their experiments that there is a limit to the quantity of Al which can be displaced on the addition of a neutral salt. Both Mattson as also Paver and Marshall stopped their leaching experiments before they could get the limiting value and consequently their results show a decrease in the sesquioxide content of the leachate with progressive leaching.

The base exchange capacity* of the original hydrogen clay, Latekujan-F is 31.0 m.e. while that of the hydrogen clay obtained after the ninth treatment has been found to be 31.6 m.e. The fact that the liberated Al ions amount to only 3.4 m.e. out of a total of 31.6 m.e. of cations exchanged indicates that H^+ ions form the major fraction of exchangeable ions present in the hydrogen clay obtained after the cycle of operations. In the original hydrogen clay, however, Al^{+++} ions constituted the main portion.

Further work on this topic is in progress.

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*As determined by Parker's $\text{BaAc}_2\text{--NH}_4\text{Cl}$ method (*J. Amer. Soc. Agron.*, 1929, 21, 1030).

CONDENSATION OF DINITROCHLOROTOLUENES WITH *p*-NITROSODIMETHYLANILINE.

By D. S. MITTAL.

Sachs and Kempf (*Ber.*, 1902, 35, 1224) prepared 2:4 dinitrobenzaldehyde and 2:4:6-trinitrobenzaldehyde by heating 2:4-dinitrotoluene and 2:4:6-trinitrotoluene with *p*-nitrosodimethylaniline in the presence of alcohol and sodium carbonate and hydrolysing the products obtained with 2*N*-nitric acid. 2:4-Dinitro-5-chlorobenzaldehyde, 3:5-dinitro-4-chlorobenzaldehyde and 3:5-dinitro-2-chlorobenzaldehyde have now been prepared by heating the corresponding toluene hydrocarbons with *p*-nitrosodimethylaniline in the presence of alcohol and sodium carbonate and hydrolysing the product so formed with 2*N*-nitric acid.

2:4-Dinitro-5-chlorobenzaldehyde was obtained as yellow needles from alcohol, m.p. 150-52°; phenylhydrazone, m.p. 217°; oxime, m.p. above 280°.

3:5-Dinitro-4-chlorobenzaldehyde was obtained as yellow crystals from alcohol, m.p. 79-80°; phenylhydrazone, m.p. 109°; benzylideneaniline, m.p. 108°; oxime, m.p. above 290°.

3:5-Dinitro-2-chlorobenzaldehyde was obtained as yellow crystals from alcohol, m.p. 78°; oxime, m.p. above 290°, benzylideneaniline, m.p. 138°.

The corresponding benzoic and cinnamic acids have been prepared from these aldehydes. They have also been reduced and the derivatives of these reduction products have been prepared.

The author's thanks are due to the Lucknow University for the facilities offered for research work and also to Dr. Sane for his kind help and guidance during the course of the work.

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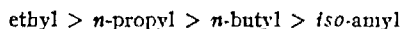




ACTION OF HALOGEN ACIDS ON ALCOHOLS • IN PRESENCE OF BENZENE.

BY S. P. WALVEKAR, N. L. PHALNIKAR AND B. V. BHIDE.

The reaction of hydrogen chloride with ethyl, *n*-propyl, *n*-butyl and *iso*amyl alcohols has been studied both in presence and absence of benzene. The rate of reaction in absence of benzene follows the order



The rate, however, increases when benzene is present and this increase is explained by solubility considerations

Experiments on esterification of organic acids in *iso*amyl alcohol with hydrogen chloride as a catalyst showed that if an inert solvent like benzene were added to the reaction mixture, the rate of esterification increased to many times its original value (Bhide and Watson, *J. Chem. Soc.*, 1927, 2102). By choosing an organic acid like picric acid as a catalyst it was shown that the velocity diminished considerably in presence of benzene (Bhide, *J. Indian Chem. Soc.*, 1930, 7, 575). On the basis of these experiments it was suggested that in presence of benzene the change in the rate of reaction is closely connected with solubility of the catalyst in benzene and *iso*amyl alcohol. Thus hydrogen chloride is sparingly soluble in benzene but very soluble in *iso*amyl alcohol. On addition of benzene the hydrogen chloride associates with the alcohol, so that the concentration of the catalyst with respect to the alcohol increases as the concentration of benzene increases, and hence the rate of esterification increases. In the case of picric acid, the acid is more soluble in benzene than in *iso*amyl alcohol so that the catalyst is associated with benzene and the concentration of the catalyst with respect to the alcohol falls as more benzene is added and therefore the velocity of esterification diminishes as the concentration of benzene increases.

As a continuation of the above work the rate of reaction of hydrogen chloride with primary aliphatic alcohols is studied in presence of benzene.

EXPERIMENTAL.

All the alcohols were dried and purified by known methods. Ethyl alcohol was dried over metallic calcium and the rest of the alcohols were dried by keeping them over anhydrous copper sulphate for several weeks.

Benzene was dried over sodium and distilled over phosphorus pentoxide. The densities and boiling points of the substances are given in the following table.

TABLE I.

Atmospheric pressure = 710 mm.

| Substance. | Density. | B.P. |
|------------------|----------|------------|
| Ethyl alcohol | 0.7803 | 76.5-77° |
| <i>n</i> -Propyl | 0.7958 | 95.5-96° |
| <i>n</i> -Butyl | 0.8008 | 116-116.5° |
| <i>iso</i> Amyl | 0.8033 | 131-132° |
| Benzene | 0.8674 | 78-78.5° |

Hydrogen chloride was prepared by the action of concentrated sulphuric acid on pure ammonium chloride and dried over phosphorus pentoxide. The reaction was carried out in pyrex bottles with tight-fitting stoppers at 70° in an electrically controlled thermostat. The vapour pressure of hydrogen chloride in the solution studied is not very high and therefore escape of hydrogen chloride is not possible.

The water formed in the reaction retards the process. Following Hinshelwood (*J. Chem. Soc.*, 1935, 599), therefore, initial rates of reaction were calculated by drawing tangents to the curves of percentage change and time. The values of the initial rate, r , expressed as percentage change per minute at 70° for ethyl, *n*-propyl, *n*-butyl and *iso*amyl alcohols are given below. The concentration C of hydrogen chloride is expressed as mols per litre of solution.

TABLE II.

| EtOH + HCl. | | | | | | EtOH + HCl in benzene. | | | | |
|--------------------|--------|-------|--------|-------|-------|------------------------|--------|--------|--------|--------|
| C | 0.1979 | 0.420 | 0.6099 | 0.690 | 1.013 | Benzene (%) | 20 | 40 | 60 | 80 |
| $r \times 10^{-4}$ | 36.67 | 59.99 | 67.50 | 70.0 | 77.50 | C (actual) | 0.2002 | 0.3002 | 0.4711 | 0.2084 |
| | | | | | | C (effective) | 0.2503 | 0.3337 | 0.4278 | 1.042 |
| | | | | | | $r \times 10^{-4}$ | 46.57 | 58.22 | 66.94 | 89.19 |

TABLE III.

| <i>n</i> -PrOH + HCl. | | | | | <i>n</i> -PrOH + HCl in benzene. | | | | |
|-----------------------|--------|--------|--------|-------|----------------------------------|--------|--------|--------|--------|
| <i>C</i> | 0.2349 | 0.5597 | 0.7754 | 1.285 | Benzene (%) | 20 | 40 | 60 | 80 |
| $r \times 10^{-4}$ | 42.97 | 54.92 | 62.10 | 71.63 | <i>C</i> (actual) | 0.1851 | 0.1969 | 0.2014 | 0.1957 |
| | | | | | <i>C'</i> (effective) | 0.2314 | 0.3281 | 0.5035 | 0.9785 |
| | | | | | $r \times 10^{-4}$ | 45.17 | 55.60 | 65.19 | 77.61 |

TABLE IV.

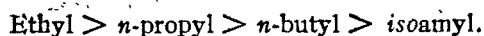
| <i>n</i> -BuOH + HCl. | | | | | | <i>n</i> -BuOH + HCl in benzene. | | | | |
|-----------------------|--------|--------|--------|--------|-------|----------------------------------|--------|--------|--------|--------|
| <i>C</i> | 0.2966 | 0.4679 | 0.7252 | 0.8847 | 1.043 | Benzene (%) | 20 | 40 | 60 | 80 |
| $r \times 10^{-4}$ | 36.06 | 47.75 | 56.26 | 60.81 | 64.61 | <i>C</i> (actual) | 0.2063 | 0.2005 | 0.2024 | 0.1991 |
| | | | | | | <i>C'</i> (effective) | 0.2588 | 0.3341 | 0.5060 | 0.9955 |
| | | | | | | $r \times 10^{-4}$ | 42.02 | 49.66 | 59.21 | 66.85 |

TABLE V.

| <i>iso</i> -AmOH + HCl. | | | | | | <i>iso</i> -AmOH + HCl in benzene. | | | | |
|-------------------------|--------|--------|--------|--------|--------|------------------------------------|--------|--------|--------|--------|
| C | 0.2182 | 0.4135 | 0.5007 | 0.6756 | 0.9616 | Benzene. (%) | 20 | 40 | 60 | 80 |
| $r \times 10^{-4}$ | 15.46 | 22.10 | 23.53 | 26.50 | 28.71 | C (actual) | 0.2176 | 0.2475 | 0.2326 | 0.2263 |
| | | | | | | C' (effective) | 0.2720 | 0.4125 | 0.5815 | 1.132 |
| | | | | | | $r \times 10^{-4}$ | 17.67 | 26.51 | 32.27 | 37.42 |

DISCUSSION.

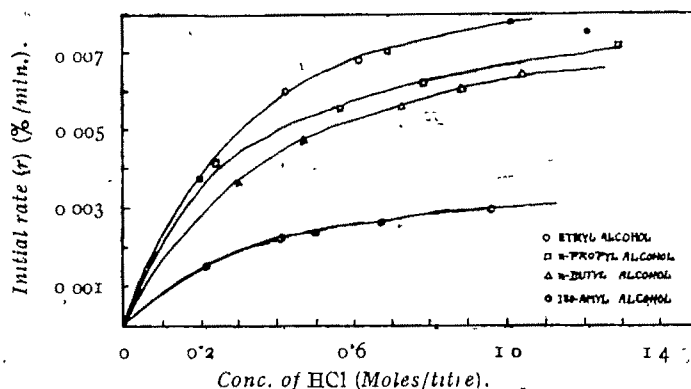
The experimental results are represented in Fig. 1. It will be observed that nature of the curve is the same as that obtained by Hinshelwood (*loc. cit.*) for the reaction of methyl alcohol with hydrogen chloride. The curves also show that the rate of reaction of hydrogen chloride with the alcohols studied follows the following order :



This is quite according to expectations. The effect of introducing a carbon atom in ethyl alcohol reduces the reactivity of the hydroxyl group,

and the reactivity goes on decreasing with the increase in the number of carbon atoms in the alcohol. This behaviour is also observed in many

FIG. 1.



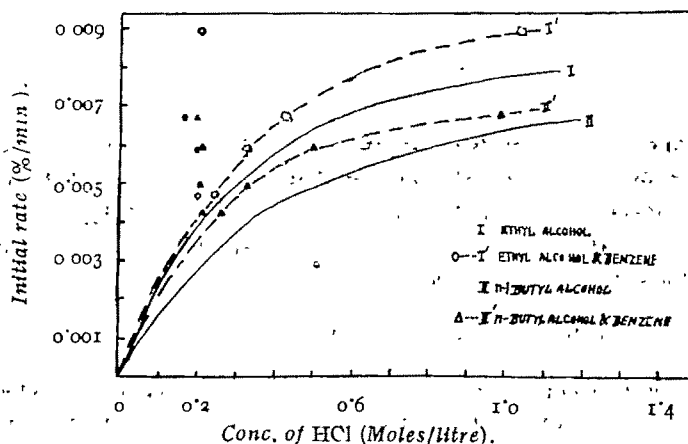
other reactions where the reacting polar group is at the end of a carbon chain. For example the rate of esterification of aliphatic acids follows the order :



This reduction in reactivity usually diminishes with increasing carbon chain and when four carbon atoms are added the reactivity is not affected at all by further increase in the carbon chain.

The effect of adding benzene to the alcohols is seen from the curves given in Figs. 2 and 3. The observed initial rates in presence of benzene increase with the increase in the concentration of benzene. This increase

FIG. 2.

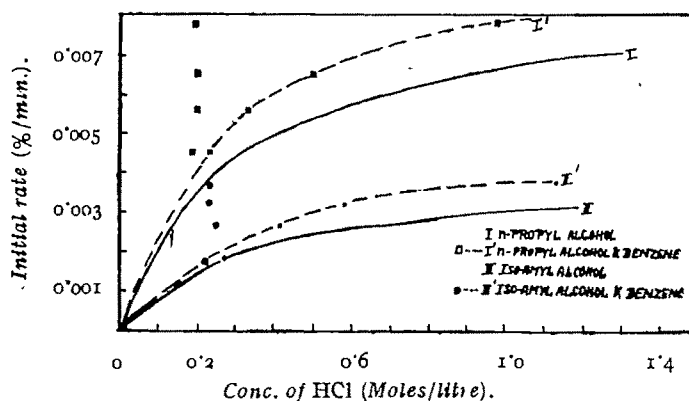


in the rates can be accounted for by assuming that as the benzene concentration increases and the solubility of hydrogen chloride in the alcohols is much greater than in benzene, the hydrogen chloride associates with the alcohol molecules. Thereby the concentration of hydrogen chloride with respect to alcohol molecules is increased. This increased concentration (C' , effective concentration) can be calculated from the following equation :

$$\text{Effective concentration} = \frac{\text{actual conc.} \times 100}{100 - \text{benzene\%}}$$

The rates of reaction expected from this effective concentration of hydrogen chloride are shown by dotted lines. It will be observed that these curves lie close to the curves showing the observed rates of alcohol and acid. The effect of addition of benzene is, therefore, to increase the effective

FIG. 3.



concentration of hydrogen chloride with respect to the alcohols and thus to accelerate the rate of the reaction. This is quite similar to the effect of benzene on the velocity of esterification of organic acids (*cf.* Bhude, and Watson, *loc. cit.*).

PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART VII.
VISCOSITY STUDIES IN MIXED SOLVENTS WITH
SOME RESINS AND CELLULOSE DERIVATIVES.

By SANTI RANJAN PALIT.

Viscosity studies in mixtures of two non-solvents having good solvent power or of one solvent and another latent solvent have been made for the following systems over a wide range of temperature and concentration: (i) ester gum in xylene-alcohol, (ii) glyptal in *n*-butyl acetate-alcohol, (iii) ethyl cellulose in cyclohexanol-cyclohexane, or alcohol-toluene and (iv) cellulose nitrate ($\frac{1}{2}$ R. S.) in alcohol-dioxane.

The viscosity curves are primarily of the same type as previously observed for shellac in suitable mixtures. The characteristic features of the curves have been summarised and generalised for different types of solutes.

In continuation of the investigation on viscosity studies of shellac in mixed solvents (Palit, *J. Indian Chem. Soc.*, 1940, **17**, 663; 1942, **19**, 207) viscosity studies in a mixture of two non-solvents having good solvent power, or of one solvent and another latent solvent (also called active solvent or coupler) of lyophilic solutes other than shellac, have been made in the present communication to test how far the results obtained therein have general validity and significance. Two other resins, *viz.*, ester gum and glyptal, have been selected as subjects of our study, since the former presents a complete contrast to shellac as being insoluble in alcohols but soluble in aromatic hydrocarbons, and since the latter is of a different type being an artificial resin, with peculiarities in solubility. Amongst the other typical lyophilic solutes, we have chosen to work with cellulose nitrate and ethyl cellulose in suitable mixtures of non-solvents. Attempt has also been made to study the protein, gliadin, the prolamine of wheat (which is soluble in a mixture of alcohol and water) but no satisfactory result has been obtained on account of the difficulties arising out of its *denaturation tendency*. Recently, however, studies in precipitation temperature of a similar protein, zein, in mixed solvents have yielded curves (*cf.* Swallen, *Ind. Eng. Chem.*, 1941, **33**, 394) similar to those we have obtained for shellac, but no viscosity data are available.

Soaps, which as lyophilic solutes form a class by themselves, have not been studied so far, due probably to the fact that there is not on record any such enhanced solvency in mixtures of solvents. The author (*Current Sci.*, 1941, **10**, 436; *J. Indian Chem. Soc.*, 1942, **19**, 271) has lately hit

upon some good mixed solvents for soaps and similar viscosity studies are contemplated. The present study might be of possible industrial importance, since all these substances are employed in the manufacture of lacquers, varnishes, printing ink, etc., viscosity control of which is a matter of considerable importance.

EXPERIMENTAL.

The experimental arrangement, procedure, method of expressing concentration, purification of solvents, etc., are the same as in the previous parts of this series of papers (*J. Indian Chem. Soc.*, 1942, **19**, 253, 266).

Preparation and Purification of Materials.—Commercial ester gum of low acid value has been finely powdered (100 mesh) and treated with about twice its weight of pure alcohol. The whole mass swells and becomes sticky by imbibition of alcohol. The sticky mass is occasionally kneaded and the whole left overnight. Three or four such extractions are made until the resin becomes free from colouring matter and acid (acid value, 1 to 2 against alcoholic potash with phenolphthalein as indicator). The resin is freed from solvent in a vacuum oven at 75° and after powdering to hundred mesh is stored in desiccators.

A commercial glyptal of low molecular weight has been used. The resin is white and hygroscopic and is stored in the powdered state in desiccators.

Ethyl cellulose of low viscosity type manufactured by Hercules Powder Co. of U.S.A. has been used.

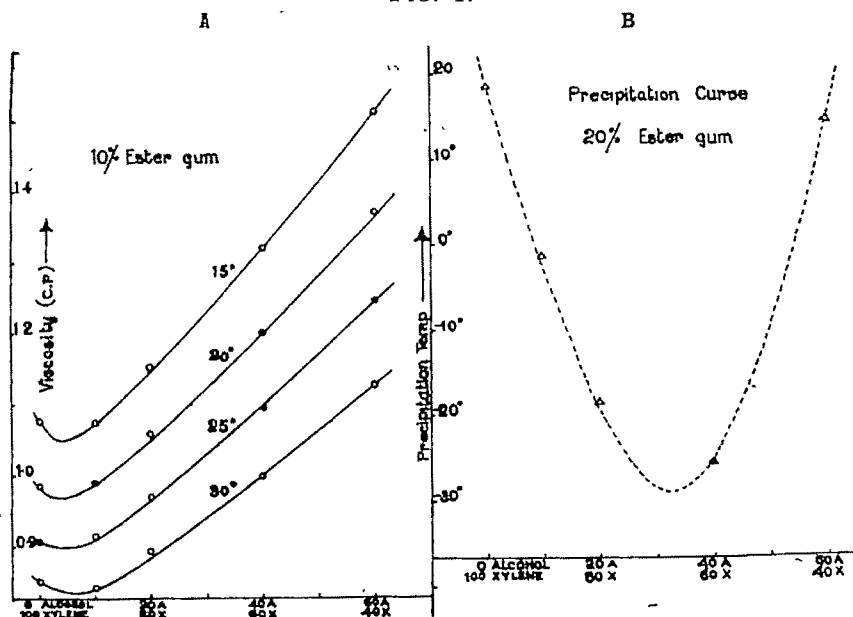
Cellulose nitrate of half-second R.S. type, manufactured by the same firm has been used. Before use, the alcohol used for damping the substance, has been driven off by heating to 105° for three hours in an air oven.

Ester Gum in Xylene-Alcohol Mixtures.

Ester gum is the glycerol ester of resin; hence the pure gum is abietic triglyceride (mol. wt., 992). The behaviour of ester gum is in many respects different from the already studied case of shellac. Its solutions are less viscous, a 50% solution having a viscosity of only about one-tenth of a poise. Further, a solution, on cooling, does not form a gel, but either separates a flaky precipitate or separates into two liquid layers. Also, due to some steric effect in the complicated molecule of the resin, it comes slowly into equilibrium with its solvent mixture, particularly at its higher

concentrations. Hence, by careful manipulation of the method of preparing the solution, it is possible to study the viscosity and other properties of such solutions as will normally separate into two liquid layers at the temperature of experiment, if allowed sufficient time. Such points as well as those, which show slight haziness during experiment as a result of separation of the solvated resin, are indicated in the graph as dark circles. These points have been included in the graph, as it has been observed that the magnitude of the viscosity change on keeping is of a smaller order.

FIG. 1.



(A) Viscosity curves in xylene-alcohol mixture.

(B) Precipitation curve in xylene-alcohol mixture.

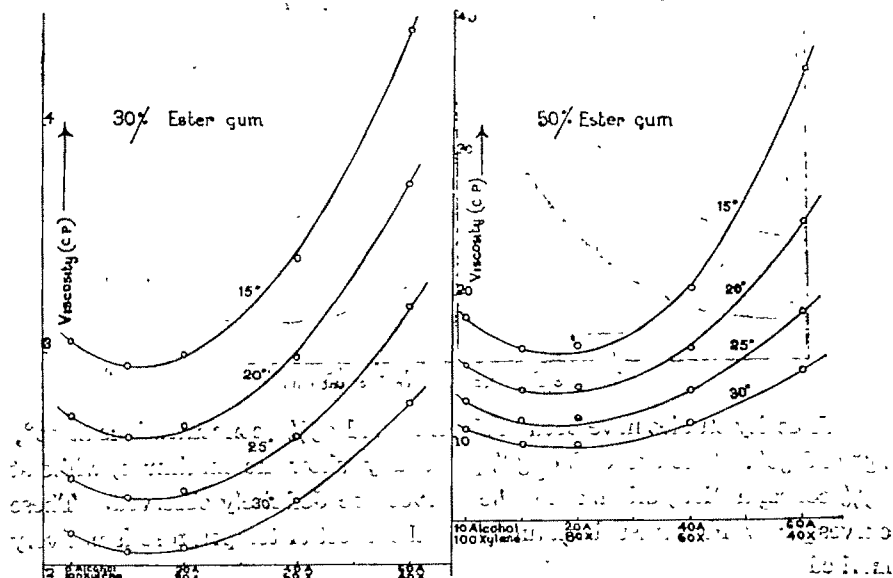
Viscosities have been studied for 10, 30 and 50% concentrations of the resin at 15°, 20°, 25° and 30°. The data are presented in Table I and viscosity curves in Figs. 1 and 2. The general nature is similar to that observed for shellac in so far as the curves are steeper at higher concentration and lower temperature. Also the minimum viscosity occurs at lesser proportion of the hydroxylic solvent than what corresponds to the minimum in the precipitation curve (so-called optimum solvent composition), and further, like all other previous cases, the minimum viscosity composition progressively approaches the optimum solvent composition with increase in resin concentration,

TABLE I.

| | | Viscosity (centipoise) at | | | | Viscosity (centipoise) at | | | |
|---------------------------|-----|---------------------------|--------|--------|--------|---------------------------|-------|-------|-------|
| Alcohol : | | 15° | 20° | 25° | 30° | 15° | 20° | 25° | 30° |
| xylene. | | Ester gum conc. = 10%. | | | | Ester gum conc. = 50%. | | | |
| 0 : | 100 | 1.077 | 0.9842 | 0.9972 | 0.8517 | 3.051 | 2.721 | 2.444 | 2.203 |
| 10 : | 90 | 1.074 | 0.9891 | 0.9143 | 0.8435 | 2.946 | 2.626 | 2.361 | 2.119 |
| 20 : | 80 | 1.152 | 1.058 | 0.9701 | 0.8943 | 2.998 | 2.679 | 2.388 | 2.144 |
| 40 : | 60 | 1.320 | 1.200 | 1.095 | 0.9903 | 3.422 | 2.985 | 2.631 | 2.348 |
| 60 : | 40 | 1.511 | 1.368 | 1.244 | 1.126 | 4.419 | 3.746 | 3.206 | 2.777 |
| Ester gum conc. = 50%. | | | | | | | | | |
| Viscosity (centipoise) at | | | | | | | | | |
| | | 15° | 20° | 25° | 30° | | | | |
| 0 : | 100 | 18.40 | 15.07 | 12.57 | 10.50 | | | | |
| 10 : | 90 | 16.20 | 13.32 | 11.14 | 9.43 | | | | |
| 20 : | 80 | 16.51 | 13.50 | 11.26 | 9.406 | | | | |
| 40 : | 60 | 20.55 | 16.32 | 13.26 | 10.95 | | | | |
| 60 : | 40 | 36.13 | 25.25 | 18.89 | 14.60 | | | | |

The precipitation temperatures have been graphically shown for 20% ester gum solutions (Fig. 1), since for higher concentrations, though the values are accurately determinable at any instant, they slowly change with time. But they all show unmistakable minima at the same region. Curve for 10% ester gum also shows minimum at this region but could not be completely determined since the two solutions at this minimum region have precipitation temperatures below our experimental range, (i.e., below -62° , as produced by solid carbon dioxide and alcohol).

FIG. 2.



Viscosity curves in xylene-alcohol mixture.

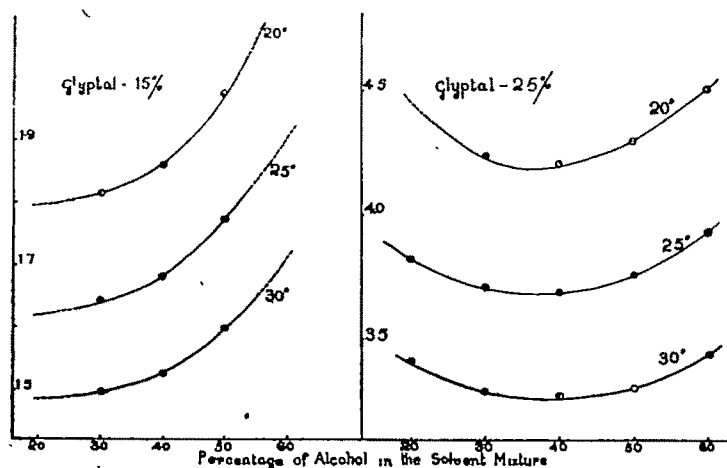
These curves have one significant point of difference from those of shellac. Here, the viscosity minimum shifts, if at all, to a very small extent with change of temperature towards a lower concentration of the hydroxylic solvent but the data are not decisive on the point.

It might be pointed out that the minimum in the precipitation curve (so-called optimum solvent composition) is richer in xylene than in alcohol, which according to the view-point previously developed by us, should be attributed to the greater solvent power of xylene than that of alcohol for the ester gum, since xylene can completely dissolve the ester gum while alcohol only swells it. Hence the fact referred to in the previous paragraph may be as follows: a lowering of temperature shifts the minimum towards a higher proportion of the more powerful solvent. This generalisation, however, requires to be tested by a study of further cases of mixed solvency.

Glyptal in Mixed Solvents.

Glyptal has been found to be completely soluble in a mixture of ethyl alcohol and *n*-butyl acetate within the approximate composition range 15:85 to 65:35. From this solubility figure as well as from the fact that alkyds are generally insoluble in aliphatic alcohols but dissolve in some esters and in many benzenoid hydrocarbons, it appears that butyl acetate is a more powerful solvent for glyptal than ethyl alcohol.

FIG. 3.



Viscosity studies have been made at 15 and 25% concentrations at 20°, 25° and 30°. The curves for 15% practically show no minimum, while at 25% concentration, minima in the curves are definitely observed. These curves show no unusual feature and the effect of temperature is not very marked.

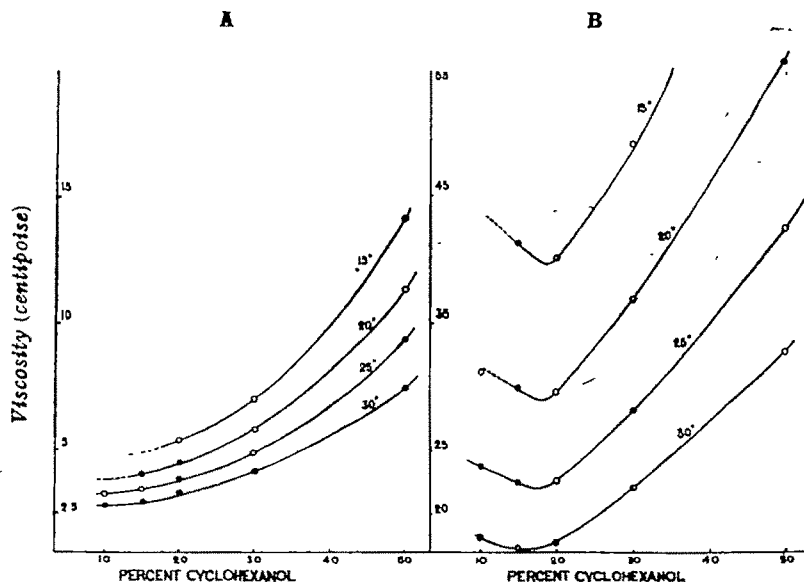
TABLE II.

| Alcohol : <i>n</i> -butyl acetate. | Viscosity (centipoise) at | | | | | |
|---------------------------------------|---------------------------|--------|--------|--------------------|-------|-------|
| | 20°. | 25°. | 30°. | 20°. | 25°. | 30°. |
| | • Glyptal conc.=15%. | | | Glyptal conc.=25%. | | |
| 20 : 80 | Insol. | Insol. | — | sl. pptn. | 3'821 | 3'406 |
| 30 : 70 | 1'813 | 1'641 | 1'497 | 4'235 | 3'714 | 3'293 |
| 40 : 60 | 1'859 | 1'679 | 1'524 | 4'205 | 3'693 | 3'273 |
| 50 : 50 | 1'976 | 1'773 | 1'597 | 4'293 | 3'766 | 2'309 |
| 60 : 40 | Insol. | Insol. | Insol. | 4'505 | 3'937 | 3'442 |

Ethyl Cellulose in Mixed Solvents.

Ethyl cellulose is insoluble in hydrocarbons as well as in alcohols but dissolves in their mixtures (Earnst *et al.*, *Ind. Eng. Chem.*, 1940, **32**, 1539). Of the solvents used here, *cyclohexane* seems to have least solvent power for the substance since it swells it to opaque cotton-like flakes, while others very

FIG. 4.



Viscosity curves for ethyl cellulose.

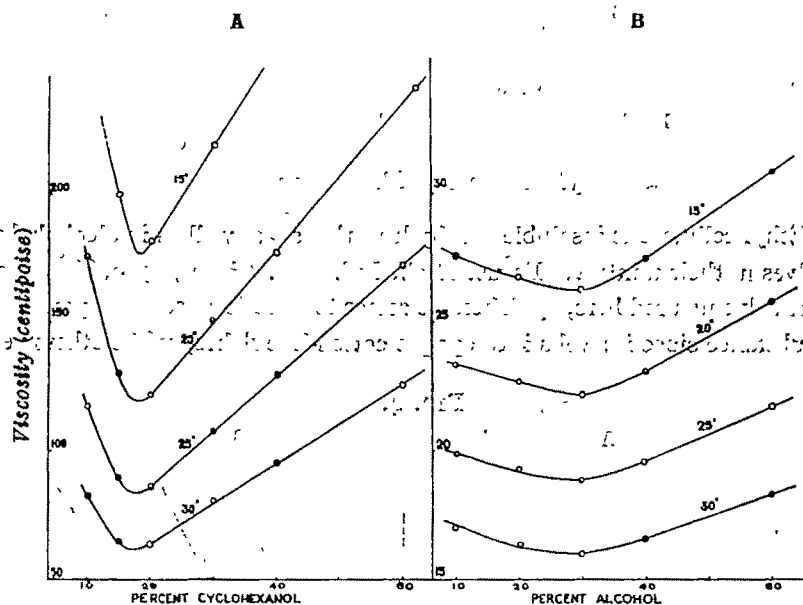
Fig. 4A—1% Ethyl cellulose in *cyclohexanol-cyclohexane*.

„ 4B—3% „ „ „ „ „

slowly produce translucent gels, alcohol being the most powerful in this respect producing practically transparent soft gel. Viscosity studies have

been made with 1, 3 and 5% concentrations of ethyl cellulose in *cyclohexanol-cyclohexane* mixtures at 15°, 20°, 25° and 30° and only 5% ethyl cellulose in *alcohol-toluene*. The results are given in the following table and are graphically represented in Figs. 4 and 5.

FIG. 5.



Viscosity curves for ethyl cellulose.

5A—5% Ethyl cellulose in *cyclohexanol-cyclohexane*.

5B—5% " " " " *alcohol-toluene*.

TABLE III.

| | | Viscosity (centipoise) at | | | | | | | |
|-------|-------|---------------------------------------|-------|-------|-------|-----------------------------|-------|-------|-------|
| | | <i>cyclohexanol</i> : 15° 20° 25° 30° | | | | 20° 25° 30° | | | |
| | | Ethyl cellulose conc. = 1%. | | | | Ethyl cellulose conc. = 3%. | | | |
| 10:90 | Pptn. | Pptn. | 3.267 | 2.838 | Pptn. | 31.18 | 23.70 | 18.06 | |
| 15:85 | Pptn. | 4.084 | 3.473 | 3.011 | 41.18 | 29.84 | 22.41 | 17.35 | |
| 20:80 | | 5.408 | 4.537 | 3.857 | 3.307 | 40.02 | 29.49 | 22.57 | 17.70 |
| 30:70 | | 7.944 | 5.843 | 4.925 | 4.176 | 48.90 | 36.76 | 28.13 | 22.06 |
| 50:50 | | 14.13 | 11.39 | 9.350 | 7.484 | 74.20 | 55.54 | 42.34 | 32.75 |

TABLE III (contd.).

| Viscosity (centipoise) at | | | | | | | | | |
|--|-------|-------|-------|--------|-----------------------------|-------|-------|-------|-------|
| <i>cyclo</i> Hexanol: 15°, 20°, 25°, 30° | | | | | Alcohol: 15°, 20°, 25°, 30° | | | | |
| <i>cyclo</i> Hexane | | | | | toluene | | | | |
| Ethyl cellulose conc.=5%. | | | | | Ethyl cellulose conc.=5%. | | | | |
| 10:90 | 238'9 | 175'8 | 117'4 | 82'47 | 10:90 | 27'58 | 23'31 | 19'90 | 17'02 |
| 15:85 | 181'2 | 121'7 | 86'14 | 63'45 | 20:80 | 26'72 | 22'68 | 19'26 | 16'32 |
| 20:80 | 219'1 | 150'8 | 108'1 | 80'28 | 30:70 | 26'25 | 22'21 | 18'85 | 16'03 |
| 30:70 | 260'5 | 177'2 | 129'9 | 95'88 | 40:60 | 27'43 | 23'08 | 19'54 | 16'58 |
| 40:60 | 349'1 | 241'5 | 172'3 | 125'80 | 60:40 | 30'76 | 25'75 | 21'66 | 18'27 |
| 60:40 | 199'7 | 130'6 | 89'8 | 64'95 | | | | | |

The general appearance of the curves is as usual, 5% and 3% curves showing definite minima at about 16-18% *cyclo*hexanol, whereas curves for 1% concentration of ethyl cellulose do not exhibit any perceptible minima. The effect of concentration of the solute is to displace the minimum towards a higher concentration of the hydroxylic solvent. This is evident by comparing the curves at 3% and 5% contents of ethyl cellulose at the same temperature. Since alcohol is a more powerful solvent for ethyl cellulose than hydrocarbons, *cyclo*hexanol, which is a hydroxylic solvent, is presumably so. This shift of minimum therefore only shows that an increase in concentration of the solute displaces it to an increased proportion of the more powerful solvent. Though the optimum solvent composition in this system could not be determined due to experimental difficulties, to be referred to later, it can be reasonably assumed from considerations of solvent power of the individual solvents, that it is certainly somewhere containing greater proportion of *cyclo*hexanol. Hence the effect of concentration becomes the same as in the previous cases, i.e., a shifting of the minimum towards the so-called optimum solvent composition.

The effect of decrease in temperature, as may be noted from the curves, is to displace the minimum towards a greater proportion of the more powerful solvent. This trend is also clearly observable from the curves for 5% ethyl cellulose in alcohol-toluene mixture (Fig. 5B), a system which is much less viscous than the previous one.

The study of precipitation or gelation temperature of this system and other systems to be described later, could not be made as the temperatures are often inconveniently low and have lesser degree of reproducibility than that of shellac.

Cellulose Nitrate in Alcohol-Dioxane.

This is virtually the same as studying the classical case of nitrocellulose in alcohol-ether (Gibson and McCall, *J. Soc. Chem. Ind.*, 1923, 39, 172r) with the advantage that the cyclic ether 1-4 dioxane is much less volatile

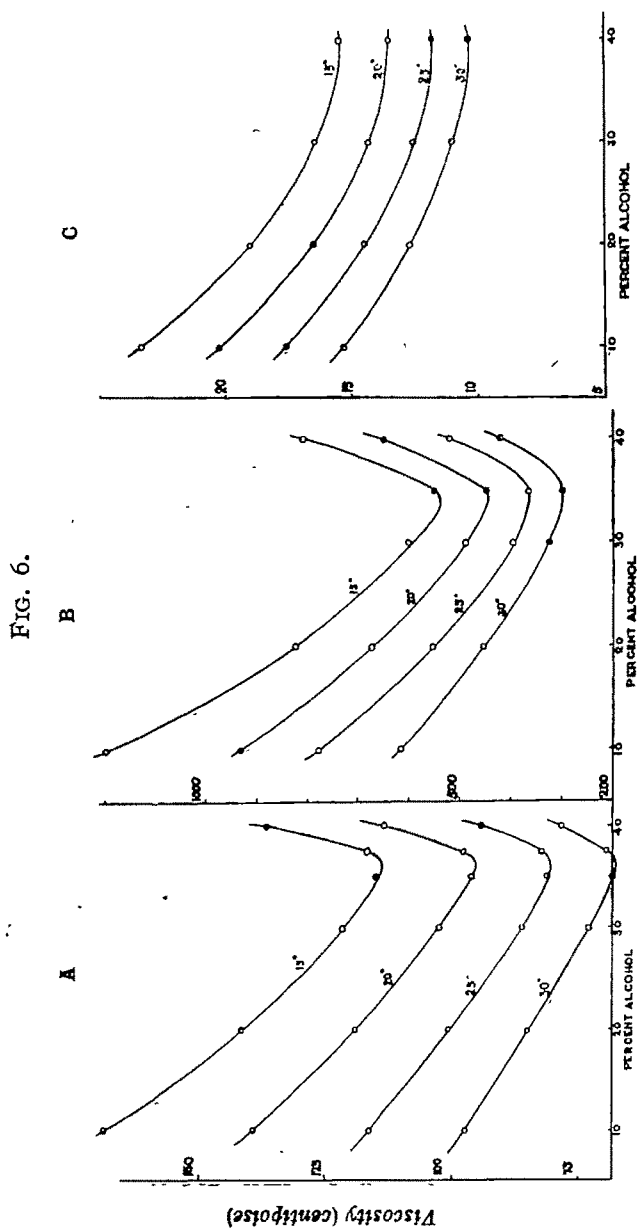


Fig. 6A—10%, Fig. 6B—15%, Fig. 6C—5% cellulose nitrate in alcohol-dioxane mixture

(b.p. 101.5°) than ordinary ether. Cellulose nitrate is soluble in this mixture containing from about 50 to 95% dioxane. From this figure on solubility, as well as from the fact that the cellulose nitrate used is of the ester-soluble type, it is easily intelligible that dioxane is a better solvent than alcohol. The above argument concerning solubility and solvent power needs elaboration. Of the two non-solvents, A and B, if A requires less B to dissolve a certain quantity of the lyophilic solute than the proportion of A, which is required by B to produce the same solubility, we shall term A, the more powerful solvent. That this is in agreement with facts is borne out by the various solubility diagrams of resins obtained previously by the author. Now, to make dioxane a solvent for nitrocellulose we have to add 5% alcohol to it, whereas to make alcohol a solvent we have to add about 50% dioxane; hence, dioxane is by far a more powerful solvent of the two.

Viscosity studies have been made for 5, 10 and 15% concentrations of cellulose nitrate at 15°, 20°, 25° and 30° (Fig. 6).

TABLE IV.

| Viscosity (centipoise) at | | | | |
|---------------------------|-------|-------|-------|-------|
| Alcohol : dioxane. | 15°. | 20°. | 25°. | 30°. |
| Nitrocellulose conc.=5%. | | | | |
| 10 : 90 | 23.37 | 20.29 | 17.61 | 15.33 |
| 20 : 80 | 19.01 | 16.50 | 14.45 | 12.69 |
| 30 : 70 | 16.48 | 14.35 | 12.54 | 11.04 |
| 40 : 60 | 15.52 | 13.54 | 11.87 | 10.39 |

| Viscosity (centipoise) at | | | | | | | | |
|---------------------------|-------|-------|-------|---------------------------|-------|-------|-------|-------|
| Alcohol : dioxane. | 15°. | 20°. | 25°. | 30°. | 15°. | 20°. | 25°. | 30°. |
| Nitrocellulose conc.=10%. | | | | Nitrocellulose conc.=15%. | | | | |
| 10 : 90 | 168.8 | 139.3 | 116.1 | 97.12 | 1195 | 931.1 | 775.7 | 613.5 |
| 20 : 80 | 141.3 | 118.8 | 100.2 | 84.55 | 820.8 | 671.9 | 549.6 | 450.7 |
| 30 : 70 | 121.1 | 102.1 | 85.90 | 72.78 | 595.3 | 485.6 | 393.4 | 322.5 |
| 35 : 65 | 114.2 | 95.76 | 80.72 | 68.13 | 548.9 | 443.0 | 361.6 | 296.3 |
| 37.5 : 62.5 | 116.0 | 97.25 | 81.94 | 68.84 | | | | |
| 40 : 60 | 136.0 | 112.6 | 93.56 | 77.69 | 803.5 | 643.9 | 515.2 | 418.6 |

The effect of increasing concentration is the same as in the previous cases. For example, there is no viscosity minimum observable at 5% concentrations, whereas minima occur at 10 and 15% nitrocellulose. The minima are at one end close to the solubility limit and more slowly drifts with increasing concentration towards the centre, i.e., a higher concentration of dioxane, presumably towards the optimum solvent composition as shown in the previous cases.

The effect of temperature is found to be the same as in the previous cases, a decrease of temperature tending to displace the minimum towards a higher proportion of the more powerful solvent. This effect is more pronounced with the curves for 15% than for 10% concentration.

CONCLUSIONS.

Both in the present as well as in the previous papers the following general trends, which we have been able to recognise in such viscosity curves have been pointed out :

The viscosity curves exhibit minimum above a certain concentration of the lyophilic solute, the sharpness of the minimum increasing with increase of concentration and decrease of temperature.

The shape of the viscosity curves as well as its dependence on concentration and temperature have already been discussed with reference to the gelation capacity of the system in a previous section of this part.

With increasing concentration, the minimum gets shifted towards, and tends to approach the optimum solvent composition.

The latter may, of course, for all practical purposes, be taken as that solvent composition at which the gelation tendency is the least, but it may be formally defined as that composition of the solvent mixture which will produce gelation with the highest concentration of the solute at any given temperature. It is borne out by observations that the relative proportion of the two solvents in the optimum composition represents their relative solvent power.

With decreasing temperature, the minimum moves slowly towards a higher proportion of the more powerful solvent or more probably towards the optimum solvent composition.

Acknowledgments are gratefully made to Dr. H. K. Sen, Director, Indian Lac Research Institute, Namkum, Ranchi, for his kind interest and helpful suggestion throughout the course of the work.

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Received May 25, 1942.

ON THE CONSTITUTION OF NATURAL COUMARINS OF *TODDALIA ACULEATA*.

BY PHANIBHUSHAN DUTTA.

From the stem-bark of *Toddalia aculeata* (i) aculeatin ($C_{16}H_{18}O_{15}$, m. p. 113°), (ii) aculeatin hydrate ($C_{16}H_{20}O_{16}$, m. p. 150°), isomeric with toddalolactone, isolated by Dey and Pillay, and (iii) a colourless substance, m. p. 239° , which has not been investigated, have been obtained. The reactions of aculeatin hydrate and toddalolactone are almost similar and they give rise to same oxidation products.

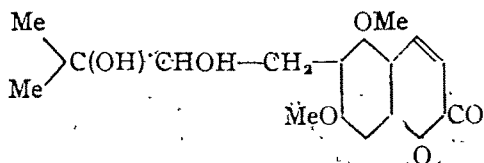
Toddalia Aculeata, Pers., (N.O. Rutaceae, Sub-family *Toddaloideae*) is a scandent shrub known to the Sanskrit writers as Kanchana (Golden) on account of the orange colour of its fruits and also called Dahana because of the pungency of its berries. The plant is distributed in the sub-tropical Himalayas from Kumaon eastwards to Bhutan at an elevation of 5,000 ft. and also in Western and Southern India and Ceylon.

The root known as Lopez root (*Toddalia radix*) has been used in the Indian Pharmacopoeia as a remedy of great value in constitutional debility and in convalescence after febrile and other exhaustive diseases. The fresh bark is administered by Tamil Physicians for the cure of a sort of remittent commonly known as "hill-fever."

Regarding the chemical constituents of Lopez root, Dymock, Warden and Hooper (*Pharmacographia Indica*, Vol I, 261) mention the presence of a resin, essential oil (smell like oil of citron) and a bitter principle.

According to Hooper (*Schimmel's Berichte*, 1893, p. 64), the essential oil consists of citronellal, linalool, and a camphor-like substance, m. p. $96.5-97^{\circ}$. The bark has been found to contain resinous matter, bitter principle, tannin, citric acid, sugar, pectin, starch etc, and yields an ash rich in manganese (Schnitzer, *Vierteljahresschrift Prakt. Pharm.*, 1862, 11, 1). An alkali-soluble glucoside believed to be hesperidin, has also been isolated (*Beih. Bot. C.*, 1902, 12, 55), but has later been proved to be diosmin (Osterle and Wander, *Helv. Chim. Acta*, 1927, 8, 519). Flückiger and Hanbury (*Pharmacographia Indica*, Vol. I, p. 262) could not detect berberine in the plant, but Perkin and Hummel (*J. Chem. Soc.*, 1895, 413) isolated a yellow crystalline hydrochloride of an alkaloid from Lopez root, which they considered to be identical with berberin hydrochloride. Dey and Pillay (*Arch. Pharm.*, 1933, 271, 477) have isolated two different alkaloids from the same source and have named them toddalin and toddalinin.

Dey and Pillay (*Arch. Pharm.*, 1933, 271, 477 ; 1935, 273, 223) further isolated from the root bark a crystalline neutral compound toddalolactone, which has been further investigated by Späth, Dey and Tyray (*Ber.*, 1938, 71, 1825) and shown to have the structure (I).



(I)

The present work describes the constituents of the stem-bark, which is also used in medicine though to a limited extent. The bark was secured from the Darjeeling District (Bengal). Three different neutral compounds have been isolated from the stem-bark (*vide* Experimental):

(1) A colourless compound, m.p. 239°, neutral to litmus, insoluble in dilute aqueous alkali and indifferent towards alcoholic ferric chloride. A detailed investigation is not possible on account of its very poor yield (0.01%).

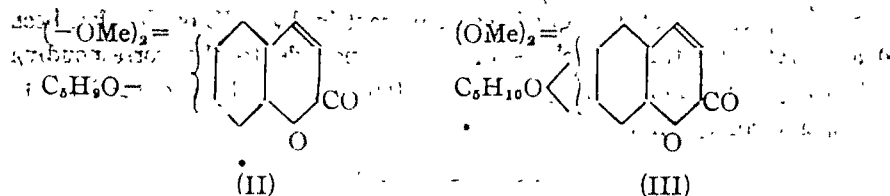
(2) The second compound, (0.06%) forming colourless plates, m.p. 173°, has been named aculeatin.

(3) A substance, m.p. 150°. It has been named aculeatin hydrate, since it is also obtained from aculeatin by prolonged treatment with dilute sulphuric acid at 100°.

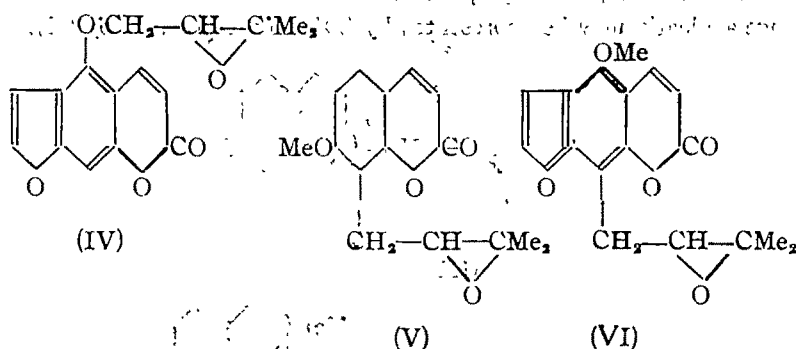
The C—H values and the molecular weight show that aculeatin has the formula $C_{12}H_{12}O_6$. Methoxyl estimation by Zeisel-Pregl-Vieböck technique proves the presence of two methoxyl groups in the molecule. Aculeatin is optically active, $[\alpha]_D^{25}$ being -16.8° in ethyl acetate. It has lactonic properties, since although aculeatin is insoluble in aqueous alkali, it readily dissolves in alcoholic alkali and acids precipitate the original compound. Hence the formula of aculeatin can be written as



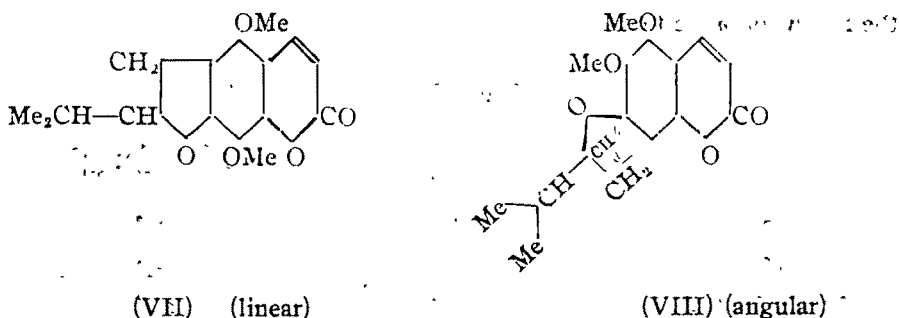
A characteristic property of coumarins is their capacity to undergo hydrolysis to a *trans*-acid when heated with alkali in presence of a trace of mercuric oxide (Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930; 7, 247). Aculeatin is found to undergo hydrolysis forming a stable acid, $C_{14}H_{12}O_7$, m.p. 171°, under the usual experimental conditions. The formula of aculeatin may consequently be further expanded to (II) or (III).



The oxygen atom in the residue, $\text{C}_6\text{H}_9\text{O}_2$ — is not ketonic or aldehydic in character since aculeatin fails to condense with the usual reagents for ketones and aldehydes. The group $\text{C}_6\text{H}_9\text{O}_2$ — has been found to occur in some natural coumarins in the form of dihydro isoprene oxide, as will be evident from an inspection of the formula of oxypeucedanin (IV), auraptene (V) and byakangelicol (VI).

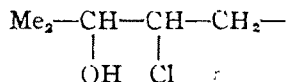


It may be further mentioned that the carbon atom in the glycidic ring is asymmetric, and consequently all these compounds show optical activity. Another possibility is the formulation of aculeatin as (VII) or (VIII), where also asymmetric carbon atoms are present. The basic ring system of

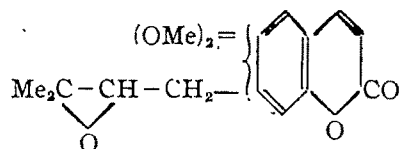


(VII) is present in nodakenin, but the angular type has not been discovered in natural products, although the possibility is not excluded.

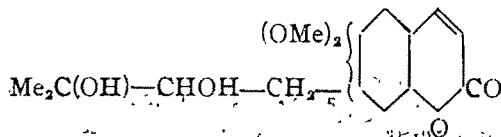
The presence of the glycidic ring present in (IV), (V) or (VI) has been demonstrated by the hydrolysis of the compounds to the corresponding dihydroxy compounds $[\text{Me}_2\text{C}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_2-]$ or conversion into the open chain system,



by means of hydrochloric acid gas. Compounds of the type (VII) and (VIII) are not known to undergo such ring-fission. Aculeatin, however, has been found to remain unaffected by treatment with 1.5% oxalic acid at 100° for 4 hours, but prolonged treatment with very dilute sulphuric acid at 100° effects a smooth hydrolysis to a colourless compound, $\text{C}_{18}\text{H}_{20}\text{O}_6$, aculeatin hydrate, m.p. 150° , which is identical with the third substance. Hence aculeatin may be represented by (IX) and its hydrate by (X).



(IX)



(X)

Aculeatin hydrate and toddalolactone are isomeric compounds having the following properties.

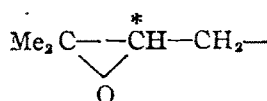
TABLE I.

| | Toddalolactone (Dey and Pillay) | Aculeatin hydrate (Present author) |
|-----------------------|------------------------------------|---------------------------------------|
| M.p. | $131-132.5^\circ$ | 150° |
| $[\alpha]_D^{25}$ | $+55^\circ$ | $+51^\circ$ |
| (M.p.) Acid phthalate | 181° | 204° |
| „ trans-Acid | 178° | $170-71^\circ$ |
| „ Diacetyl | $111-112^\circ$ | 127° |

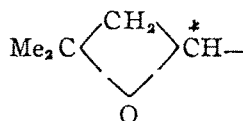
Aculeatin hydrate forms a diacetyl derivative showing the presence of two alcoholic OH groups. The fact that only one molecule of phthalic anhydride combines with one of aculeatin hydrate suggests that one of the two OH groups is tertiary in character.

Aculeatin hydrate is found to undergo degradation by means of chromic acid giving rise to acetone (identified as dibenzal acetone) indicating the presence of $\text{Me}_2\text{C}<$ group in the side chain. It will not be unreasonable to attach one OH group to the central C atom of the isopropyl group to make it tertiary, $\begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Me} \end{array} < \text{OH}$, to explain the formation of the mono acid, phthalate, and of acetone by degradative oxidation.

The position of the second OH group with respect to the tertiary OH group will depend on the nature of the oxide-ring in aculeatin, which may be formulated as a 1:2-oxide or 1:3-oxide as shown below:



1:2-Oxide



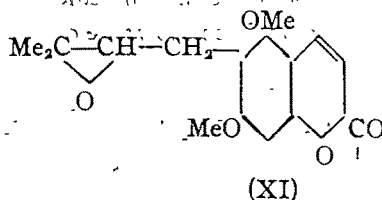
1:3-Oxide.

The former, however, would be expected to furnish a glycol $\text{Me}_2\text{C}(\text{OH})\text{---CHOH---CH}_2\text{---}$ and the latter a glycol $\text{Me}_2\text{C}(\text{OH})\text{---CH}_2\text{---CH}(\text{OH})\text{---}$ on hydrolysis. Aculeatin hydrate furnishes on oxidation by Criegee's reagent (Criegee, *Ber.*, 1931, **64**, 260) a compound, m.p. $142^\circ\text{---}142.5^\circ$, which analyses for $\text{C}_{13}\text{H}_{12}\text{O}_5$, and produces *p*-nitrophenyl hydrazone, m.p. 213° , and reduces ammoniacal silver nitrate, thus showing that aculeatin possesses the 1:2—oxide structure. The reactions of aculeatin hydrate and toddalolactone (Späth, Dey and Tyray, *loc. cit.*) are almost similar and they give rise to same oxidation products, *e.g.*, the aldehyde (m.p. $141.5^\circ\text{---}142.5^\circ$, *p*-nitrophenylhydrazone, m. p. 213°); and the ketone (m.p. 119° , semicarbazone, m. p. 206.9° , *p*-nitrophenylhydrazone, m.p. 209°), under the influence of fused zinc chloride or 2% hydrochloric acid at 140° .

A specimen of toddalolactone was obtained from Dr. B. B. Dey, to whom my best thanks are due, and the aldehyde and ketone obtained from it had identical m.p. (m.p. of the derivatives is also the same). The mixed melting points were also the same. The chemical evidence is definitely in favour of the identity of aculeatin hydrate and toddalolactone.

It has been possible to isolate a compound, m. p. 150° , from the sample of toddalolactone kindly supplied by Dr. B. B. Dey. The melting point of this remained undepressed when mixed with aculeatin hydrate (m. p. 150°). This suggests that either toddalolactone contains aculeatin hydrate as an impurity, or there is a possibility of a new type of isomerism which admits of a transformation from Dey's type to aculeatin hydrate by a simple process of recrystallisation from ethyl acetate and adding petroleum ether (b. p. $30-40^{\circ}$) as diluent, the process being repeated several times. It may therefore be remarked that repeated recrystallisations of aculeatin hydrate do not alter its m. p. (150°).

Whatever may be the causes of the difference between toddalolactone and aculeatin hydrate, there cannot be any doubt as to the correct structure of aculeatin, which must be represented by (XI).



EXPERIMENTAL.

Isolation of Aculeatin and Aculeatin hydrate.

Finely powdered dry stem bark of the plant *Toddalia Aculeata* (Pers.) (Y Kg.) was extracted with ether for 16 hours in a Soxhlet apparatus and three neutral compounds were isolated from the ethereal extract.

(1) The filtered extract was concentrated to about 60 c.c., and ether (40 c.c.) added as diluent and this was kept in a frigidaire. Crystals began to appear after 3 days. After 13 days the crystals were collected at the pump, and washed with a little ether. These crystals were then boiled with ethyl acetate, when a small portion remained insoluble. The ethyl acetate insoluble portion was removed by filtration, and on crystallising twice from a mixture of chloroform and absolute alcohol, the m. p. was found to be $233^{\circ}-234^{\circ}$. Further crystallisations raised the m. p. to $238^{\circ}-239^{\circ}$. It formed small colourless rectangular plates.

It is not soluble in ether, petroleum ether, ethyl acetate, acetone. It is soluble in chloroform and sparingly in absolute alcohol, yield 0.01%. It is insoluble in dilute alkali and gives no colouration with ferric chloride. [Found: C, 70.25; H, 5.93; OMe, 22.7. Calc. for $C_{16}H_{16}O_4$: C, 70.58; H, 5.88; OMe, 22.8 per cent based on $C_{14}H_{10}O_2$ (OMe) $_2$].

(2) The ethyl acetate solution was concentrated to a small volume, and cooled, the crystals which separated were collected and purified by recrystallisation once from benzene, and twice from ethyl acetate when the m. p. became constant at 113° (corrected), yield of aculeatin was 0.06%. Aculeatin forms colourless plates, $[\alpha]_D^{25} = -16.8^{\circ}$. It is highly soluble in benzene, ethyl acetate, chloroform, alcohol, moderately soluble in ether, acetone and practically insoluble in petroleum ether. It dissolves in concentrated sulphuric acid with orange colour. It is neutral to litmus and gives no colouration with ferric chloride and is also insoluble in 1% sodium hydroxide solution. [Found: C, 66.28; H, 6.18; OMe, 20.95; M.W (cryoscopic in benzene), 294; $C_{16}H_{18}O_5$ requires C, 66.20; H, 6.20; OMe, 21.30 per cent. M.W. 290].

(3) The oil left after the separation of the crops of crystals was subjected to steam distillation. A small amount of essential oil distilled over. The steaming was continued for 6 hours and the apparatus was allowed to stand over night. Next morning the yellow aqueous supernatant liquid was decanted out from the distilling flask and evaporated to dryness on a water-bath, when the residue became oily and highly viscous. This was cooled, scratched, adding a little ether from time to time. By this operation the viscous mass solidified gradually, but no crystals could be observed under microscope. This solidified mass was now introduced into a 100 c.c. conical flask, a little methyl alcohol added and allowed to stand over night. Next morning the solid was filtered at the pump and freed from adhering oil. The product was crystallised from chloroform, benzene, ethyl acetate and ultimately subjected to high vacuum distillation (170° - $180^{\circ}/0.1$ mm.) and the distilled product was again crystallised from benzene and ethyl acetate successively. Aculeatin hydrate, thus obtained, had m.p. 150° (corrected).

The oily residue left at the bottom of the steam-distillation flask was dissolved in a solvent (ether and a little methyl alcohol). This solution was allowed to stand for 3 days when a crop of crystal separated out. These crystals were also subjected to the same process of purification. It had m.p. 150° and was identical with aculeatin hydrate. The mother liquors from these two crops of crystals were allowed to stand in the cold, when another crop of crystals separated out; purified in the manner described above, it had the same m.p. of 150° . Mixed melting point was also exactly the same. The total yield of aculeatin hydrate (m.p. 150°) is 4.28 g. from 1 kg. of the stem bark; or 0.428%.

Aculeatin hydrate, thus purified (m.p. 150°), formed ill-defined prisms, $[\alpha]_D^{25} = +56.9^{\circ}$ in chloroform solution. It is highly soluble in chloroform, and moderately in benzene and ethyl acetate, and practically insoluble in

petroleum ether. It dissolves in concentrated sulphuric acid with an orange colour, and gives no colouration with ferric chloride. It dissolves in 5% alkali and is precipitated unchanged by hydrochloric acid. (Found: C, 62.23; H, 6.41; OMe, 20.49. $C_{18}H_{20}O_6$ requires C, 62.33; H, 6.49; OMe, 20.13 per cent).

Hydrolysis of Aculeatin: Formation of Aculeatin Hydrate.—In methyl alcoholic solution, aculeatin was hydrolysable in presence of 2*N*-sulphuric acid or alkali at the room temperature, but the hydrolysis was far from being complete. The following method was found suitable for the hydrolysis

A solution of aculeatin (0.1 g.) in minimum quantity of rectified spirit was diluted with water (10 c.c.) and refluxed on a wire gauge for 8½ hours with two drops of sulphuric acid (2*N*). The clear solution was evaporated on water-bath until oily drops separated out. This was now cooled, and extracted with chloroform (twice) and also with ether (twice). These chloroform and ethereal extracts were washed with a little water separately. Finally the ethereal and the chloroform extracts were mixed together, dried over anhydrous sodium sulphate, filtered and evaporated nearly to dryness. The solid product, thus obtained, was twice crystallised from ethyl acetate, m. p. 149.5° (mixed m.p. with aculeatin hydrate remained undepressed), yield 0.052 g.

Diacetyl aculeatin hydrate was obtained from aculeatin hydrate as usual using acetic anhydride and sodium acetate. It crystallised from benzene and petroleum ether mixture, m.p. 127°. [Found: OMe, 16.28. $(OMe)_2C_{14}H_{12}O_2(OAc)_2$ requires OMe, 15.82 per cent].

On deacetylation with alcoholic sodium hydroxide, it regenerated aculeatin hydrate, m.p. 149.5°.

Preparation of the Ketone $C_{18}H_{18}O_5$ from Aculeatin and Aculeatin Hydrate—Aculeatin (0.1 g.) was heated with fused zinc chloride (1 g.) in a metal-bath at 140–45° for 1 hour. The mixture was poured into water containing a few drops of dilute hydrochloric acid and the whole was extracted with ether. Crystals were collected after concentrating the ethereal solution and purified by high vacuum distillation, m.p. 119.5°.

Aculeatin hydrate (0.3 g.) was heated with aqueous hydrochloric acid (2%, 5 c.c.) in a sealed tube at 140° for 4 hours. The product of reaction was extracted with ether and the ethereal extract washed with water, dried over anhydrous sodium sulphate and concentrated. The crystals were recrystallised from a mixture of ether and petroleum ether and were distilled at 160–70°/0.1 mm., and finally recrystallised twice from ether,

m.p. 119-20° (corrected), yield 0.11 g. (Found: C, 66.15; H, 6.28. Calc. for $C_{16}H_{16}O_5$: C, 66.21; H, 6.21 per cent).

The ketone, prepared from a specimen of toddalolactone, melted at 119-120° (mixed m.p. of the two remained undepressed).

The semicarbazone of the ketone melted at 209° after recrystallisation from rectified spirit. (Found: N, 11.85. Calc. for $C_{17}H_{21}O_5N_3$: N, 12.1 per cent). The semicarbazone of the ketone obtained from Dey's toddalolactone also melted at 207.8° (mixed m.p. almost the same).

The *p*-Nitrophenylhydrazone of the ketone was crystallised from rectified spirit, m.p. 209°. (Found: N, 9.97. $C_{22}H_{23}O_5N_3$ requires N, 9.88 per cent). The *p*-nitrophenylhydrazone of the ketone obtained from Dey's toddalolactone had m.p. 210°, mixed m.p. same.

trans-Coumaric acid derivative of Aculeatin Hydrate.—Aculeatin hydrate (0.1 g.) was heated with sodium hydroxide solution (10 c.c., 0.2 N) with a trace of mercuric oxide for 2 hours under reflux. The solution was filtered to remove mercuric oxide, and the filtrate was concentrated on a water-bath, cooled and acidified with dilute hydrochloric acid. The precipitate was collected, washed with water and was crystallised from dilute methyl alcohol, m.p. 170-171° (decomp.) [Found: C, 58.50; H, 6.8. $C_{16}H_{22}O_7$ requires C, 58.8; H, 6.75 per cent].

The acid phthalate of aculeatin hydrate was prepared as usual from aculeatin hydrate and phthalic anhydride by heating at 135° for 6 hours. After the reaction the mass was dissolved in dilute ammonia and extracted with chloroform to remove the unchanged aculeatin hydrate. The ammoniacal solution was acidified with dilute hydrochloric acid and extracted with chloroform. The acid phthalate, obtained by evaporating chloroform, was crystallised from 70% alcohol, m.p. 204°. (Found: C, 63.25; H, 5.4. Calc. for $C_{24}H_{24}O_8$: C, 63.15; H, 5.26 per cent).

Oxidation of Aculeatin Hydrate with Cr_2O_3 .—A solution of aculeatin hydrate (1 g.) in glacial acetic acid (15 c.c.) with chromic acid (0.5 g.) dissolved in 20 c.c. of 50% acetic acid was allowed to stand at the room temperature for 60 hours in a well-stoppered flask. The reaction mixture was first distilled until 5 c.c. distillate were collected in a receiver containing 5 c.c. methyl alcohol (Merck), 4 drops of freshly distilled benzaldehyde and 4 drops of 10% sodium hydroxide solution. Due to the presence of acetic acid carried over during the distillation, the expected condensation did not occur. Hence this distillate was treated with calcium carbonate to eliminate the acetic acid and distilled again. The distillate (5 c.c.) was collected and made alkaline with 3 drops of 10% sodium hydroxide solution when dibenzalacetone separated in fine needles; recrystallised from 50%

methyl alcohol, m. p. $111.5-112^{\circ}$, and identified as dibenzalacetone by mixed melting point.

Oxidation of Aculeatin Hydrate to the Aldehyde, $C_{13}H_{12}O_8$, by Lead Tetraacetate.—A solution of aculeatin hydrate (0.45 g.) in glacial acetic acid (7 c.c.) and a solution of lead tetraacetate (0.8 g.) in glacial acetic acid (25 c.c.) were allowed to stand for 17 hours at the room temperature, and finally warmed to 40° for 15 minutes. Water (10 c.c.) was then added and the solution was concentrated under reduced pressure and 10 c.c. water again added, when crystals separated. These were filtered at the pump, and crystallised from a mixture of benzene and petroleum ether, m.p. $142-142.5^{\circ}$ (corrected). It distilled at $150-160^{\circ}/0.1$ m.m. (Found: C, 62.76; H, 5.0. $C_{13}H_{12}O_8$ requires C, 62.90; H, 4.83 per cent).

The aldehyde, prepared from toddalolactone, also melts at $141.5-142.5^{\circ}$ (mixed m.p.)

My grateful thanks are due to Dr. P. K. Bose for his kind interest and encouragement during the course of these investigations and also placing the resources of his laboratory at my disposal.

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART VIII, A DISCUSSION ON THE VISCOSITY OF RESINS, CELLULOSE DERIVATIVES, ETC IN MIXED SOLVENTS.

By SANTI RANJAN PALIT.

Viscosity data obtained for lyophilic solutes, *e.g.*, resins, cellulose derivatives, etc. in mixed solvents have been examined from theoretical and experimental considerations. It has been shown that the results are qualitatively in agreement with the classical equations on viscosity. The conditions for the occurrence and position of the minimum viscosity have been discussed and the results have been generalised in the shape of a rule, deductions from which have been shown to be in accord with the available data.

The present communication is an analysis of the results presented in some previous papers (Palit, *J. Indian Chem. Soc.*, 1940, **17**, 663; 1942, **19**, 207) of this series, to correlate them with the available data on a common background. Mention may, however, be made of the work of various authors who attempted to correlate the solvent power and viscosity of solutions of resins and nitrocellulose with the oxygen content of the solvent, the presence of polar groups, molecular volume, etc. with only limited success. The author's main observations and results have been summarised in the previous paper and discussion will be made without any further reference to them.

Mathematical Analysis.

It is of interest to examine how far our result can be fitted into the existing equations of viscosity. Let us assume that the viscosity curve of the pure solvent mixture be of a simple type, without exhibiting maximum or minimum, as given by the equation of Kendall and Munroe (*J. Amer. Chem. Soc.*, 1917, **39**, 1802).

$$\eta_0^{\frac{1}{3}} = x\eta_1^{\frac{1}{3}} + (1-x)\eta_2^{\frac{1}{3}} \quad \dots \quad (1)$$

where x is the mol-fraction of the component whose viscosity is η_1 , η_2 is the viscosity of the other component, and η_0 that of the mixture. If now progressively increasing amounts of a lyophilic solute are added to the solvent mixtures, each point on the curve would rise up vertically corresponding to

* For discussion, *vide* Bancroft "Applied Colloid Chemistry" 1942, p. 381, Doolittle, *Ind. Eng. Chem.*, 1938, **30**, 189

a rapid increase of viscosity with increase of concentration. Various equations have been proposed to represent viscosity variation with concentration, of which we shall examine the most classical one—the exponential equation of Arrhenius, which can be put as

$$\log \eta = \log \eta_0 + kc \quad \dots (ii)$$

where η is the viscosity of the solution and η_0 , that of the solvent mixture, c represents concentration of the solute and k is a constant. Combining these two equations, we get a generalised equation representing at any composition of the solvent mixture any concentration of the solute. The combined equation is

$$\log \eta = 3 \log \{px + q(1-x)\} + kc \quad \dots (iii)$$

where p and q stand for $\eta_1^{\frac{1}{3}}$, and $\eta_2^{\frac{1}{3}}$ respectively. The constant k has certainly not the same value for all compositions of the solvent mixture, but is an unknown function of x . So we may put $\phi(x)$ for k when we get

$$\log \eta = 3 \log \{px + q(1-x)\} \phi + (x).c$$

This equation can show a minimum with respect to x -axis, when the first partial differential of viscosity vanishes, i.e., $\partial\eta/\partial x = 0$. Now differentiating with respect to x , we get (iii, a) which for minima in the viscosity curves, gives equation (iv).

$$\frac{1}{\eta} \cdot \frac{\partial\eta}{\partial x} = \frac{3(p-q)}{px + q(1-x)} + c \cdot \frac{\partial\phi}{\partial x} \quad \dots (iii, a)$$

$$\text{or} \quad c \cdot \frac{\partial\phi}{\partial x} = \frac{3(q-p)}{px + q(1-x)} \quad \dots (iv)$$

This equation gives the concentration, c of the solute which will produce minimum viscosity at any given composition, x of the solvent mixture. This equation cannot be utilised, unless ϕ is explicitly known as a function of x , which can only be done by empirical means. But it can elucidate one important point, that the viscosity minimum approaches the optimum composition with increase in concentration of the solute. In other words, we have to find out the condition under which c becomes very high. Evidently, from equation (iv) when

$$\frac{\partial\phi}{\partial x} \rightarrow 0, \quad c \rightarrow \infty.$$

But $\partial\phi/\partial x = 0$ is the condition for a minimum in $\phi(x)$. Then it follows that to whatever extent the concentration may increase, the viscosity minimum

would tend to approach the composition for which the Arrhenius constant $k = \phi(x)$ is a minimum. A minimum in k implies the optimum solvent composition by definition. Hence, we have thus theoretically derived, within the very restricted validity of the starting equations (i) and (ii) our main experimental observation that the viscosity minimum does not occur at a fixed solvent composition, but tends to approach the optimum solvent composition with increase of solute concentration. Hence, not viscosity, as is often loosely stated, but *some function of viscosity*, which is unaffected by the concentration of the solute, should be found out for comparison of solvent power. Baker (*cf.* Doolittle, *Ind. Eng. Chem.*, 1938, **30**, 195, 199) adopted the constant $ak = \left(\frac{\partial \log \eta}{\partial c} \right)_{c \rightarrow 0}$ in his parabolic equation, $\eta = \eta_0(1 + ac)^4$ and McBain utilised the average Arrhenius constant,

$$k = \frac{x}{c} \log \eta / \eta_0$$

for dilute solutions, to compare the solvent power for nitrocellulose (*J. Phys. Chem.*, 1926, **30**, 312).

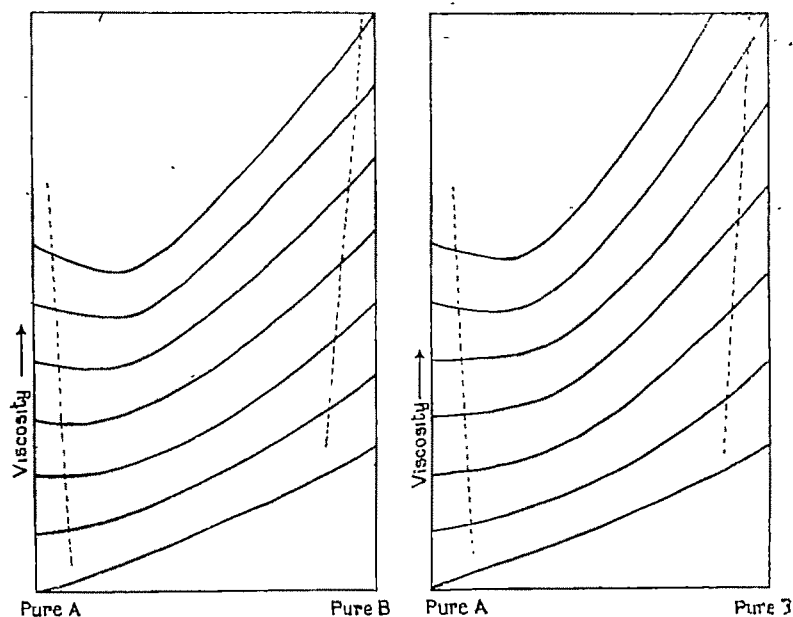
Discussion of the Position of the Viscosity Minimum.

The viscosity curves of the pure solvent mixtures we have used, have mostly no maximum or minimum point, but conform to the usual type of having a slight sag, *i.e.*, convex towards the x -axis, as shown in Fig. 1 (lowest curve). Let us now consider what happens when progressively increasing amounts of a lyophilic solute are added to the solvent mixtures. Each point of the curve would move up vertically corresponding to a rapid increase of viscosity with increase of concentration. The rate of upward rise, however, is not the same at every point on the curve. As will be apparent from any series of experimental viscosity curves already given, the two extremes rise more rapidly than the central portions. As a result, as the concentration increases, there comes a point where a minimum is observed.

The whole thing is made more clear graphically by some imaginary curves as shown in Fig. 1. Between the dotted lines and the two vertical axes is the insoluble region, the slight slant of the dotted lines implying the experimentally observed fact that, the higher the concentration of the lyophilic solute, the broader is the available solvent composition range. Two types of minima are observable. In Fig. 1 (a) is shown the minimum first making its appearance at one extreme of the available composition and gradually moving towards the central sector with increase of concentration. In Fig. 1 (b), the minimum is first noticeable somewhere in the central

portion of the solvent compositions. This happens when due to the slow upward motion of the left hand compositions, the flattening of the curve first takes place right in the workable region.

FIG. 1.



Viscosity curves of a solvent mixture with increasing conc. of the lyophilic solute.

The above qualitative description leads to a very important deduction. We have proved conclusively both theoretically and experimentally that increase of concentration always shifts the minimum viscosity towards the optimum solvent composition. This qualitative picture shows that there is more chance for the minimum to make its appearance near the less viscous component; or more precisely stated, the minimum has to move from the less viscous to the more viscous component. Hence, we come to the very important conclusion that *the minimum viscosity should usually lie between the pure less viscous component and the optimum solvent composition, and should tend to move towards the latter composition with increasing solute concentration.*

This conclusion will be referred to later as *the rule of minimum viscosity*, applicable to lyophilic solutes in mixtures of two latent solvents, or of one solvent and another latent solvent. Presumably we shall look for a perfect validity of the rule in solvent mixtures whose viscosity-com-

position curve shows only a sag but no maximum or minimum. It is also assumed that no chemical combination of the solvents in the accepted sense takes place, for example, aniline-acetic acid type mixtures do not come under this rule.

That the viscosity of the individual solvents is an important factor was, perhaps, realised by McBain (*loc.cit.*). It was not realised, however, that whatever disparity in viscosity lies between the two individual latent solvents, the viscosity minimum is bound to appear with high concentration of nitrocellulose.

The rule of minimum viscosity may be more concretely put as follows. We have already shown (*vide* Part IV) that the ratio of the solvent powers gives the optimum solvent composition. Hence, if there are two non-solvents, A and B, showing mixed solvent effect, and if the viscosity of A is less than that of B, then two cases may arise depending on the relative solvent powers of A and B.

Corollary A. (1)—If the solvent power of A is greater than that of B, then the viscosity minimum lies close to the pure solvent, A, and never beyond 50% of A. The more powerful is A in comparison with B, the more will be the closeness of the minimum towards the pure A side.

A. (2)—If the solvent power of A is less than that of B, the viscosity minimum may be anywhere between pure A and somewhere containing more than 50% of A, depending on the relative solvent power of the two.

A special case arises when A is a true solvent and B is a coupler (latent solvent), the expected results being given as follows:—

Corollary B. (1)—If $\eta_A < \eta_B$, the viscosity minimum will be in the first half very close to A, and with increasing concentration of the solute, will move towards a higher percentage of the coupler.

B (2)—If $\eta_A > \eta_B$, the viscosity minimum may remain anywhere from the lowest possible to a very high percentage of the coupler (*i.e.*, up to the optimum solvent composition), and will travel towards a lower percentage of the latent solvent with increase in concentration of the solute.

Experimental Test of the Rule of Minimum Viscosity.

It is interesting to test how far these generalisations are borne out by available experimental data. Previous data on resins in mixed solvents are absent. So far the author's data on resins and cellulose derivatives are concerned, there is no single exception to this rule, the viscosity minimum being always found to lie between the pure low viscous components and the optimum solvent composition (*vide* Table I).

TABLE I.

| Solute conc. | Less viscous solvent (A). | More viscous solvent (B) | * Relative solvent power. A:B. | Observed position of minimum (%B). |
|----------------|---------------------------|--------------------------|--------------------------------|------------------------------------|
| Shellac. | | | | |
| 25 to 35% | Acetone | Water | 86 : 14 | 7-12 |
| 35 to 45% | Acetone | Glycol | 36 : 64 | 14-25 |
| 45 to 50% | Methyl acetate | Glycol | 30 : 70 | 42-46 |
| 25 to 35% | Acetone | Alcohol | 20 : 80 | 15-30 |
| Ester Gum. | | | | |
| 30 to 50% | Xylene | Alcohol | 68 : 32 | 2-20 |
| Glyptal. | | | | |
| 25% | Butyl acetate | Alcohol | >50% | About 35 |
| Ethylcellulose | | | | |
| 3 to 5% | cycloHexane | cycloHexanol. | >50% B. | 15-18 |
| 5% | Toluene | Alcohol | „ | About 30 |
| Nitrocellulose | | | | |
| 10 to 15% | Alcohol | Dioxane | >>50% B | About 65 |

* *i.e.*, optimum solvent composition A : B

Viscosity studies of cellulose nitrate and acetate are available to some extent though such studies, as pointed out by Sproxton (*Third Report on Colloid Chemistry*, 1920, p. 84), are scanty before 1920. A good amount of data accumulated in the next few years, but they are of questionable reliability, particularly after the demonstration by McBain (*loc. cit.*) of the various sources of error. We choose from among the data of this period to discuss those of Mardles (*J. Soc. Chem. Ind.*, 1923, **42**, 207T; *J. Chem. Soc.*, 1923, **123**, 1951; 1924, **125**, 2244) on cellulose acetate and those of McBain and co-workers (*loc. cit.*) on cellulose nitrate in the light of our theory. Since viscosity data in two non-solvents are scarce, we shall make a test of corollary B of the minimum viscosity rule for solvent-coupler mixture. We shall first make clear our reasoning by illustration with a typical case. Suppose, we take the case of ethyl acetate-alcohol solutions of nitrocellulose. Viscosity of the ester is 0.441 (25°) and that of alcohol is 1.05 (at 25°). Now, ethyl acetate, a true solvent, is by far more powerful than the latent solvent, alcohol and hence, the optimum solvent composition would contain far in excess of 50% of the ester, say, 70 : 30 proportion of ester : alcohol. Hence, according to our view, the

viscosity minimum will always lie between the pure low viscosity solvent and the optimum solvent composition, *i.e.*, it must be between 0 to 30% alcohol depending on the concentration of the solute. Of course, the value 30 has here been a reasonable estimate only, but if the relative solvent power is determined by the method proposed by us, or by any other suitable method, it is possible to fix it definitely. At all events, it can never exceed 50% alcohol. From Mardles data very few cases of solvent-active solvent mixtures are available for testing our theory (particularly, corollary B). Our main contention that the viscosity minimum lies between the pure less viscous solvent and the optimum solvent composition is, however, borne out by his data and curves (ether-alcohol, cyclohexanone-benzyl alcohol, acetone-alcohol, etc.) where it is observed to lie between the pure less viscous solvent and the composition having maximum solvent power. The data of McBain and co-workers, though involving a variety of solvents, are hardly utilisable for such test, since it is impossible to find out the position of the minimum for their data on viscosity and Arrhenius constant at only two or three solvent compositions. But, in the main, no palpable exception to our rule could be found.

Some recent precise data on nitrocellulose ($\frac{1}{2}$ " R.S.) (*cf.* Doolittle, *loc. cit.*) may be used for testing the rule of minimum viscosity. Doolittle has studied 8% nitrocellulose in 29 solvent combinations of which 13 are ester-alcohol mixtures. Since methanol itself is a solvent for this type of nitrocellulose (for actual value *cf.* McBain, Grant and Smith, *J. Phys. Chem.*, 1934, **38**, 1217) and so cannot be regarded as a latent solvent, this rule cannot be tested in its combination with ester. Leaving out the 3 cases using methanol, all the other combinations have the ester as the less viscous component, and alcohol as the higher viscous component. Hence, according to our theory, the viscosity should either continually rise with increase of alcohol, or should show a minimum nearer the pure ester end. All the experimental curves without exception conform to this expected behavior. The viscosity data for methanol with methyl, ethyl or isopropyl acetate do not show a minimum up to 50% methanol. Perhaps, it is above 50% methanol, which may show that methanol is a more powerful solvent for $\frac{1}{2}$ " R.S. cellulose nitrate than the esters. This is confirmed by independent measurement of solvent power by dilution ratio method of the same system when it is found that the addition of methanol up to 50% (data above 50% not available) continually increases the solvent power of the ester.

In the same paper, 11 cases of ketone (solvent)-alcohol (coupler) mixture are studied, all of which, in agreement with our theory, either show a

continuous rise of viscosity with increase in alcohol, or show a minimum at small proportion (5-30%) of alcohol. Doolittle could not explain why acetone fails to show a minimum viscosity, whereas our views completely explain this supposed anomaly. If Doolittle would have increased the concentration of nitrocellulose, minimum would have been observed slowly approaching towards the optimum solvent composition. The extremely low viscosity of acetone (0.32 c.p.) is admittedly responsible for such late appearance of the minimum viscosity.

Of the remaining two cases with butanol and cellosolve or methyl cellosolve, the latter system behaves in perfect agreement with our theory. There is, however, one real exception, *i.e.*, the case of cellosolve-butyl alcohol. Cellosolve is less viscous than butyl alcohol and certainly has stronger solvent power than butyl alcohol. Hence, according to our theory either the viscosity would rise with butyl alcohol, or it should show a minimum at somewhere less than 50% butyl alcohol. The given data show that up to 60% butyl alcohol the viscosity continually decreases. We are now forced to admit it as a real departure from our rule, unless by actual experiment we are able to demonstrate a non-validity of our fundamental condition—the absence of maximum or minimum in the pure solvent mixture. From general considerations it will easily appear that only a pronounced minimum towards the alcohol side, or maximum towards the cellosolve side in the viscosity curve of the pure solvent mixture can bring forth such departure from the rule of minimum viscosity. It may be pointed out that such singular point in viscosity curves is very common in such mixture of two hydroxylic solvents (Jaegar, "Second Report of Viscosity and Plasticity", 1938, p. 80; Spels, *Trans. Faraday Soc.*, 1936, **32**, 530; Hatschek, "Viscosity of Liquids", 1928, p. 136). Any way, it is of real significance that the rule can pass a test of 27 cases with only one doubtful failure. Some very recent data by Ware and Teeters (*Ind. Eng. Chem.*, 1939, **31**, 738, 1118) on viscosity of different concentrations of nitrocellulose in ester-alcohol allow a further test of our rule of minimum viscosity. Seven pure esters and seven pure alcohols have been studied in 36 combinations, each combination being provided with data for more than two concentrations of nitrocellulose, and in all these cases not a single instance is observable where the minimum or the viscosity variation is in the opposite sense to that demanded by our theory. (The value 73.2 in pure *n*-propyl acetate with 11% nitrocellulose is perhaps a misprint, as appears from the general trend of its adjoining figure; otherwise this constitutes a serious discrepancy to our theory).

*Effect of Concentration and Temperature on the Position of
Minimum Viscosity.*

It has already been demonstrated that the effect of increasing concentration is to shift the minimum viscosity towards the optimum solvent composition. But according to the rule of minimum viscosity, the viscosity minimum is always towards the low viscosity side of the optimum solvent composition. Hence, we may state that the effect of increasing concentration is to displace the minimum towards a higher proportion of the more viscous solvent.

A lowering of temperature, so far its effect on viscosity is concerned, is normally equivalent to an increase of solute concentration. Hence, on similar grounds we may state that with decrease of temperature the viscosity minimum shifts towards a higher proportion of the more viscous component. The nearer are the systems to the gelation region, the more pronounced will be the effect. These deductions from theory are in good agreement with our observations.

It would have been interesting to study rubber, which also shows pronounced augmentation of solvent power by addition of hydroxylic non-solvents (*cf.* Gee, *Trans. Faraday Soc.*, 1940, **36**, 1162, 1171; Kemp and Peters, *Ind. Eng. Chem.*, 1941, **33**, 1264) to test our view point, but unfortunately no viscosity data in mixed solvents are available.

Critical Examination of the Theory.

There are two fundamental and crucial points in our arguments. Firstly we have defined the optimum solvent composition as that composition of the solvent mixture which requires the highest concentration of the lyophilic solute to just produce gel at any given temperature. Since the composition, as defined above, is difficult of experimental determination, we have chosen to call that composition as the optimum one, which has the least tendency to gel-formation on cooling. Such an assumption has been found to be approximately justified on experimental grounds. It then follows from definition that since this composition can stand highest concentration of solute without gelling, the viscosity minimum will always tend to approach this composition with increase of solute concentration and should ultimately coincide with it in the limiting case of using of the highest workable concentration of the solute which just gives gel. Hence, it is clear that the assumption that the viscosity minimum will drift towards and finally coincide with the optimum solvent composition, is a sound one based on perfectly

logical theoretical considerations and is amply supported by experimental data. Secondly, it will be evident by following the arguments that we advanced when deducing the minimum viscosity rule in conjunction with its accompanying series of curves (Fig. 1) that, if the viscosity minimum has to occur and to drift towards the optimum composition, the simplest geometrical possibility is that the minimum should first make its appearance by the low viscosity side of the optimum solvent composition. Hence, it is established that if the basic conditions (*i.e.*: no maxima or minima in the viscosity of the pure solvent mixture, no chemical combination, etc.) are satisfied, the rule of viscosity minimum follows as a logical deduction.

In attempting to apply it to actual cases we have made the assumption that the proportions of the individual solvents at the optimum composition respectively represent their solvent power. We have already discussed in a previous paper (Part IV) the validity of such an assumption and may only state that so far, we have not met with any case in conflict with this. Experiments are, however, in progress to make a crucial unambiguous test of such an hypothesis on the lines pointed out earlier, results of which only can pronounce the final verdict. But it must be pointed out that the admissibility or otherwise of such an assumption in no way affects the validity of our rule. Only it will not remain as easy as now to foretell from solvent power data (preferably, by gelation or precipitation method) the expected range in which to expect the viscosity minimum, and its direction of drift with concentration of the lyophilic solute.

It should be recognised that our theory is only applicable to cases of mixtures of two complimentary latent solvents or of a solvent and a coupler, but does not extend to mixtures of pure solvents. This limitation is due to the fact that our assumption that an optimum solvent composition exists, may not always be true in these latter cases. It may quite happen that two good solvents on mixing may antagonise each other's solvency in such a way that a mixture may gel at a lesser concentration of the solute than the individual pure solvents. Under such circumstances, viscosity maximum may be observable and this may perhaps be the cause of the viscosity maximum of shellac dissolved in a mixture of two good solvents, alcohol and acetic acid (*cf.* Mardles, *loc. cit.*).

Irregular Solvents and the Rule of Minimum Viscosity.

Two sharply differentiated types of cases may be recognised from geometrical consideration. Firstly, if the minimum is between the optimum solvent composition and the low viscosity component, geometrical considerations show that the rule will be obeyed throughout; if the minimum of the pure

mixture is on the other side of the optimum composition, there is hardly any chance of the rule being valid. For the case of maximum, just the reverse holds with somewhat lesser degree of certainty. These deductions are so easily made from a consideration of the geometrical possibilities of the curves similar to those in Fig. 1 that detailed discussions are omitted.

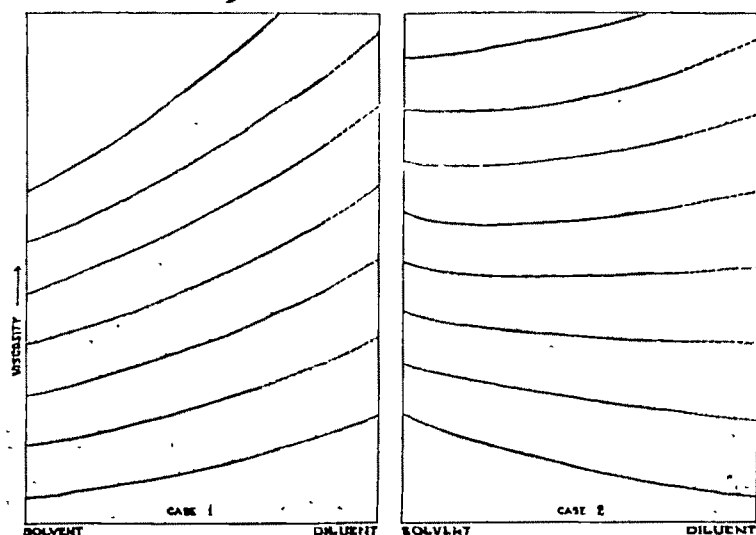
According to Mardles (*loc. cit.*) the colloid only makes prominent any peculiarity in the viscosity curve of the pure solvent mixture. In other words if two solvents show viscosity maximum in mixture, on adding a lyophilic colloid the maximum will be more prominent.

This rule evidently cannot hold good in mixtures of two complimentary latent solvents or of a solvent and a coupler as we have established, both theoretically and experimentally, that at sufficient concentration of the lyophilic solute a minimum in viscosity curve is bound to appear independent of the nature of the viscosity curve of the pure solvent mixture. The example of acetone-water mixture is a very apt one to illustrate the inadequacy of Mardles' view. This mixture is well-known (Int. Critical Tabl. Vol. V. p. 22) to show viscosity minimum when cellulose acetate, cellulose nitrate or shellac is dissolved in it.

Latent Solvent and Diluent.

A diluent is a substance whose solvent power is practically nil in comparison with a true solvent. Hence, there is no optimum solvent composition except practically on the pure solvent itself. It therefore, follows from what we have said above, that the minimum, if any, should tend to

FIG. 2.



Viscosity change of a solvent-diluent mixture with increasing concentration of nitrocellulose

approach the pure solvent with increasing concentration. It is not true that on replacing a part of the solvent by a diluent, the viscosity of the nitrocellulose solution always increases as proved from the following simple consideration. If the solvent-diluent viscosity curve is of the simple type showing no maximum or minimum, two possibilities (Fig. 2) may occur depending on whether the diluent has higher or lower viscosity. As more and more solute is added, the two curves slowly go up and assume the successive forms as shown. Evidently, in type 1, diluent will always be found to increase the viscosity, whereas in type 2, the diluent with increasing concentration of nitrocellulose first decreases the viscosity then may show minimum viscosity and finally at high concentrations of nitrocellulose shows the usual behaviour. Since most investigations on nitrocellulose, have so far been carried out at high viscosity, these points have been missed. That actually at a lower concentration of nitrocellulose, the curve for a low viscosity diluent tends to show minimum, is clearly brought out by the quite recent data of Ware and Bruner (*Ind. Eng. Chem.*, 1940, **32**, 78) for nitrocellulose in isobutyl acetate-toluene mixture as shown in the table below (see particularly data for 8% nitrocellulose).

TABLE II.

| isoButyl acetate toluene. | Viscosity (sec.) at 25° for nitrocellulose conc (g./100 cc.) | | | |
|------------------------------|--|------|-------|-------|
| | 7 g. | 8 g. | 9 g. | 10 g. |
| 100 : 0 | — | 42.0 | 54.0 | 71.0 |
| 80 : 20 | — | 41.5 | 55.6 | 78.5 |
| 90 : 40 | 38.8 | 48.4 | 62.7 | 89.7 |
| 50 : 50 | 39.0 | 52.3 | 71.9 | — |
| 40 : 60 | 46.3 | 67.3 | 101.0 | — |

Further, it is interesting to observe from a table compiled by McBain (*J. Phys. Chem.*, 1934, **38**, 1217) that in perfect agreement with our views, toluene (non-solvent) shows improved solvency (presumably viscosity lowering) with alcohol for an alcohol-soluble nitrocellulose, whereas with acetone, it does not give any optimum composition. It may be noted that the viscosity of the diluent (toluene) is lower than that of alcohol but much higher than that of acetone. So, the distinction between an active solvent and a diluent is, that for the latter in combination with a pure solvent the optimum solvent composition is practically the pure solvent itself, while for the former it contains some proportion of the active solvent. Hence, the current idea that a diluent always increases the viscosity is found to be misleading at times.

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PHOTO-OXIDATION OF QUININE.

By T. L. RAMA CHAR.

The photo-oxidation of quinine hydrochloride by uranyl nitrate, sodium vanadate and potassium dichromate has been studied. Differences have been obtained for the velocity of photo-reduction of vanadate by quinine in *d* and *l*-circularly polarised light.

Complex Formation.—Uranyl nitrate enhances the rotation of quinine hydrochloride, $C_{20}H_{24}N_2O_2$, HCl , $2H_2O$. Measurements of the rotation of these mixtures, keeping the concentration of quinine hydrochloride constant, showed that the rotation of the mixtures attained a maximum value for mixtures of the composition quinine-4-uranyl; further increase in concentration of uranyl had no effect on the maximal rotation. Assuming that for these optimum mixtures (*i.e.* for which the maximal rotations just begin) complex formation is complete, *i.e.* concentration of complex = concentration of quinine, the dissociation constant of the complex

$$K = \frac{[\text{Complex}]}{[\text{Quinine-complex}] \times [\text{uranyl-complex}]}$$

was calculated according to the method described for tartaric acid-uranyl nitrate mixtures in a previous paper (Rama Char, *J. Indian Chem. Soc.*, 1942, 19, 351). The results are given below.

TABLE I.

Length of solution = 2.5 cm. $\lambda = 5893\text{\AA}$. Temp. = 25°.

Conc. of quinine hydrochloride = 0.025M. Conc. of quinine hydrochloride = 0.012M.

| Conc. of uranyl. | Obs. rotation | Conc. of complex | K. | Conc. of uranyl. | Obs. rotation. | Conc. of complex. | K. |
|------------------|---------------|------------------|-----|------------------|----------------|-------------------|-----|
| 0.100M | -0.60° | 0.025M | | 0.050 | -0.30 | 0.013 | |
| 0.050 | -0.54 | 0.019 | 102 | 0.028 | -0.26 | 0.008 | 100 |
| 0.025 | -0.49 | 0.014 | 115 | 0.012 | -0.23 | 0.005 | 102 |
| 0.013 | -0.44 | 0.008 | 94 | 0.006 | -0.21 | 0.003 | 110 |
| — | -0.36 | — | — | — | -0.18 | — | — |
| Mean value | | | | | | | 104 |

There is concordance in the values of *K* and the sign of rotation of the complex is the same as that of quinine.

Photoreaction.—The complex obtained by the addition of uranyl nitrate to quinine hydrochloride is photo-sensitive and undergoes reduction in the ultraviolet, quinine being oxidised and the uranyl salt reduced to the uranous state: $U^{VI}_{(yellow)} \rightarrow U^{IV}_{(green)}$. The experimental arrangement for studying the photoreaction was the same as that described in a previous paper (Rama Char, *J. Indian Chem. Soc.*, 1941, **18**, 507).

The reaction was followed by estimating the uranous content by the König-Marten spectrophotometer. For this purpose standard uranyl solution was completely reduced in an atmosphere of CO_2 to the uranous state by adding the calculated amount of titanous chloride. The uranous concentration in the blackish green solution thus obtained was estimated according to the method described in a previous paper by the author (Rama Char, 1942, *loc cit.*).

Different sets of mixtures of uranous solution and quinine hydrochloride were then made up, the concentration of quinine being the same for a set but varying from one set to another. The absorption of these mixtures in the blue region was then measured spectrophotometrically. The molecular extinction coefficient, ϵ is given by,

$$\epsilon = (\log \tan \theta_2 - \log \tan \theta_1) / c.d.$$

where θ_2 and θ_1 are the spectro-readings with solution and water respectively, c , the molar concentration of solution and d , the length of solution in cm. The measurements showed that the absorption of the mixture in each set was independent of the concentration of quinine and depended only upon the uranous concentration. The results obtained for a few typical mixtures are given below.

TABLE II.

Length of solution = 0.5 cm. $\lambda = 4916\text{\AA}$.

| Conc. of uranous. | (log tan θ_2 - log tan θ_1) in conc. of quinine. | | |
|-------------------|---|---------|---------|
| | 0.025M. | 0.013M. | 0.006M. |
| 0.020M | 0.515 | 0.515 | 0.515 |
| 0.013 | 0.372 | 0.372 | 0.372 |
| 0.006 | 0.213 | 0.213 | 0.213 |
| 0.003 | 0.139 | 0.147 | 0.139 |

The concentration of uranous when plotted against (log tan θ_2 - log tan θ_1) gave a straight line (diagram not shown), and from this the concentration of uranous in any unknown mixture could be found out by knowing the spectro-reading.

There is no dark reaction in 24 hours and the photoreaction is zero-molecular with respect to uranyl. The results obtained are given below. dx/dt refers throughout to the number of g. mols transformed per minute.

TABLE III.

Radiation = complete ultraviolet. $p_H = 3$ to 4. Temp. = 25°.

| Conc. of quinine | Conc. of uranyl. | I_{abs} | dx/dt | $k = (dx/dt)/I_{abs}$ |
|---------------------|---------------------|------------|----------------------|------------------------|
| 0.025M | 0.500M | 20070 ergs | 5.0×10^{-5} | 25.0×10^{-10} |
| " | 0.100 | " | 5.0 | 25.0 |
| " | " | 10380 | 2.5 | 24.0 |
| " | 0.050 | 17300 | 4.3 | 24.9 |
| 0.013 | " | " | 4.3 | 24.9 |
| " | 0.025 | " | 4.3 | 24.9 |
| " | " | 8650 | 2.2 | 25.4 |
| 0.006 | 0.013 | 17300 | 4.2 | 24.3 |
| 0.003 | 0.010 | " | 4.3 | 24.9 |
| 0.001 | 0.004 | " | 4.3 | 24.9 |
| " | 0.002 | " | 4.2 | 24.3 |

The results show that in spite of the large variation in the concentration of the reactants, the velocity of the reaction is simply proportional to the intensity of the light absorbed by the complex:

$$dx/dt = k \times I_{abs}, \text{ where } k = 24.8 \times 10^{-10} \text{ (mean value).}$$

Quinine Vanadate Sol.

Quinine vanadate sol was prepared by peptising the freshly precipitated quinine vanadate obtained by the addition of quinine hydrochloride to sodium meta-vanadate. It was then filtered when a colourless sol was obtained. This was quite stable for several days and did not coagulate.

This sol is photo-sensitive to ultraviolet light (3130 Å) and undergoes reduction when exposed to this radiation, quinine is oxidised and vanadium reduced from the pentavalent to the quadrivalent state. The reaction was followed by estimating the vanadium (as V^{IV}) according to the method of Furman (*Ind Eng. Chem.*, 1925, 17, 314). There is no dark reaction in 18 hours and the photoreaction is zero-molecular with respect to pentavalent vanadium. The results obtained are given below.

TABLE IV.

$\lambda = 3130\text{\AA}$. $p_H = 7.1$. Temp. = 25° . $k = (dx/dt)/I_{abs} \times [\text{sol}]$.

Conc. of quinine : conc. of NaVO_3 in sol = 1:7.

| Conc. of sol. as V^v . | I_{abs} | dx/dt | k . | Quantum efficiency (γ). |
|------------------------------------|-----------|----------------------|----------------------|-------------------------------------|
| 0.023M | 4560 ergs | 7.9×10^{-8} | 7.5×10^{-8} | 0.05 |
| 0.012 | " | 3.9 | 7.1 | 0.03 |
| 0.023 | 9120 | 15.8 | 7.5 | |

The velocity of the reaction can be expressed by the equation,

$$dx/dt = k \times I_{abs} \times [\text{sol}], \text{ where } k = 7.4 \times 10^{-8}.$$

The quantum efficiency of the photo-process is small.

Reaction in Circularly Polarised Light.—Quinine vanadate sol exhibits circular dichroism in the ultraviolet (3130\AA), the anisotropy factor g being positive. This means that the molecular extinction coefficient of the sol in l -circularly polarised light is greater than that in d -light, and therefore, the velocity of the photoreduction of the sol in l -light is expected to be greater than that in d -light. The experimental results conform to these expectations. Circularly polarised light was obtained by the combinations of a Glans polarising prism and a Carl Zeiss quarter-wave plate. The circular dichroism was measured according to a method involving the sensitive Moll thermopile relay system with a Zernicke galvanometer. (The details are described in a paper to be published shortly). The values obtained for the circular dichroism of the sol and for the velocity of the photoreduction are given below.

TABLE V.

Conc. of sol as $\text{V}^v = 0.023\text{M}$ $\epsilon_l = \text{Mol.}$
extinction coeff. in l -circularly polarised light. $\epsilon_d = \text{Mol.}$ extinction
coeff. in d -circularly polarised light.
Other conditions same as in Table
IV.

| Wave-length. | $g = (\epsilon_l - \epsilon_d) / \frac{1}{2}(\epsilon_l + \epsilon_d)$. |
|-------------------|--|
| 3130 \AA | +0.011 |

TABLE VI.

Conc. of sol as $\text{V}^v = 0.023\text{M}$
 $\lambda = 3930\text{\AA}$. Other conditions same
as in Table IV.

| Polarised light. | | I_{abs} . | dx/dt . |
|------------------|--|-------------|------------------------|
| l -circular | | 1380 ergs | 2.7×10^{-6} . |
| d " | | " | 1.8 |

The velocity of the reaction in l -light is greater than that in d -light, and the difference in the value of dx/dt is very large.

Quinine Dichromate Sol.

Quinine dichromate sol was prepared, as in the case of quinine vanadate sol by peptising the freshly precipitated quinine dichromate obtained by the addition of quinine hydrochloride to potassium dichromate. It was then filtered when a yellow or orange coloured sol was obtained. This was quite stable for several days and did not coagulate.

The sol is photo-sensitive to ultraviolet (3130\AA) as well as to visible light (4060\AA and 4360\AA) and undergoes reduction when exposed to these radiations. Quinine is oxidised and dichromate reduced: Cr^{VI} (yellow) \rightarrow Cr^{III} (green). The reaction was followed by the iodimetric method for the estimation of dichromate. There is no dark reaction in 15 hours, and the photoreaction is zero-molecular with respect to dichromate.

The experimental results given in Table VII below show that they are of the same type as those obtained for the photo-reduction of quinine vanadate sol.

TABLE VII.

$\lambda = 3130\text{\AA}$. $p_{\text{H}} = 5.3$. Temp. = 25° . $k = (dx/dt)/I_{\text{abs}} \times [\text{sol}]$.
Conc. of quinine : conc. of $\text{K}_2\text{Cr}_2\text{O}_7$ in sol = 1:3.

| Conc. of sol as dichromate. | I_{abs} | dx/dt | k | Quantum efficiency (γ) |
|--------------------------------|------------------|----------------------|----------------------|------------------------------------|
| 0.012M | 9950 ergs | 3.6×10^{-6} | 3.0×10^{-8} | 0.012 |
| 0.006 | „ | 1.7 | 2.9 | 0.006 |
| 0.012 | 5280 | 1.8 | 2.8 | |
| „ | 3290 | 1.2 | 3.0 | |

Contrary to the observations of Forbes *et al* (*J. Amer. Chem. Soc.*, 1932, **54**, 960) it has been found that the sol undergoes photoreduction in blue light. Tables VIII and IX give the results obtained in the violet and blue regions.

TABLE VIII.

$\lambda = 3060\text{\AA}$. Other conditions same as in Table VII.

| Conc. of sol. | I_{abs} | dx/dt | k | γ |
|---------------|------------------|----------------------|----------------------|----------|
| 0.012M | 8650 ergs | 2.7×10^{-6} | 2.6×10^{-8} | 0.008 |
| 0.006 | „ | 1.4 | 2.7 | 0.004 |
| 0.012 | 6490 | 2.0 | 2.6 | |
| „ | 4320 | 1.4 | 2.7 | |

TABLE IX.

 $\lambda = 4360\text{\AA}$. Other conditions same as in Table VII.

| Conc. of sol | I_{abs} | dx/dt | k | γ |
|--------------|------------------|----------------------|----------------------|----------|
| 0.012M | 7780 ergs | 2.4×10^{-6} | 2.6×10^{-6} | 0.007 |
| 0.006 | „ | 1.2 | 2.6 | 0.004 |
| 0.012 | 4840 | 1.5 | 2.6 | |

Tables VII, VIII and IX show that the quantum efficiency of the photo-process is small ; it decreases with increasing wave-length of the radiation.

The velocity of the photoreduction of quinine dichromate sol in the ultraviolet, violet and blue regions can be expressed by the equation :

$$dx/dt = k \times I_{\text{abs}} \times [\text{sol}].$$

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STUDIES ON ADSORPTION IN RELATION TO CONSTITUTION. PART I. ADSORPTION OF ALKALOIDS BY SILICA GEL.

BY B. P. GYANI AND P. B. GANGULY.

Adsorption of a number of alkaloids from alcoholic solutions on silica gel has been studied. Considerable amounts of the alkaloids are adsorbed and the adsorption process follows Freundlich's equation. The attainment of equilibrium has been found to be a slow process. The temperature coefficients of adsorption are generally large. Similarly constituted alkaloids have given comparable adsorption coefficients. A parallelism between physiological activity and adsorption is also observed.

The adsorption of individual alkaloids on different surfaces has frequently been observed. Thus Moravek (*Ark. Kem. Min. Geol.*, 1923, 8, No. 30, 1), found that brucine dissolved in benzene or toluene was strongly adsorbed on fused *d*-tartaric acid; the amount adsorbed was ten times as large as that required for the formation of a monomolecular layer. Graham and Carr (*J. Amer. Chem. Soc.*, 1924, 46, 695) reported that nicotine compounds of calcium were present in tobacco grown on soil rich in lime. This apparent union of calcium and nicotine was explained by Chapin (*ibid.*, 1925, 47, 892) as an adsorption process. This view was confirmed by Thatcher's (*ibid.*, 1924, 46, 1539) observation that nicotine was completely removed when shaken with calcium carbonate. Sartorius and Ottemeyer (*Z. unters. Lebensm.*, 1929, 58, 353) compared the adsorptive capacity of various brands of powdered and granular charcoal for caffeine. Most of the caffeine was adsorbed from solution immediately; on longer contact the adsorption curve reached a maximum which later on followed a slight decline. Rise of temperature accelerated the adsorption but decreased the quantity. The adsorption from coffee infusions was less than from pure caffeine solutions; the colour and aroma of the infusions were not perceptibly affected by the process. The adsorption of quinine on active charcoal (norit) was studied by Guerrant and Salmon (*J. Biol. Chem.*, 1928, 80, 67). The p_H of the solution considerably modified the adsorption of quinine hydrogen sulphate. Malquori (*Anal. Chim. Appl.*, 1932, 22, 448) studied the adsorption of the hydrochlorides of nicotine, caffeine and quinine on silica gel and on the hydroxides of aluminium, chromium and iron. The adsorption in each case was found to be considerable. Silica gel was found to be much more active towards the nicotine salt than towards quinine hydrochloride. Hydrolytic adsorption of the latter was not observed.

From the examples stated above, it is evident that the adsorption of alkaloids vary considerably both in the nature and extent of the process. A detailed study of the adsorption of alkaloids on silica gel has been undertaken in the present investigation.

EXPERIMENTAL.

The adsorption of morphine, nicotine, strychnine, brucine, quinidine, cinchonidine, quinine, piperine and caffeine from alcoholic solutions has been determined. The solutions used were of comparable concentrations and contained 0.5 g. of the pure alkaloid in 100 c.c. of absolute alcohol, except in the case of strychnine of which a saturated solution was used. Usually 25 c.c. of the solutions were shaken with 2 to 5 g. of silica gel in well stoppered bottles and left for a sufficiently long time to attain equilibrium. The amount of adsorption was determined by analysis before and after the addition of the gel. The gel used in these experiments was a sample obtained from the Silica Gel Corporation. To activate the gel it was first washed with distilled water for several days till free from acid and then dried at 100°. The gel was next heated to about 300° and a current of carbon dioxide-free air was drawn through it for three hours. The gel activated in this way was stored in a desiccator.

Estimation of alkaloids, specially when present in mixtures is a matter of some difficulty. As pointed out by Prescott, estimation with Wagner's reagent or Meyer's reagent is not reliable as the composition of the precipitated iodides depends on concentration, temperature, time and other factors (*cf. Ber.*, 1899, **32**, 2871, *Z. anal. Chem.*, 1900, **39**, 201; Hezzig, *Arch. Pharm.*, 1922, **289**, 249). In the present investigation, however, estimation of only single alkaloid is required. Direct titration against standard acid with a properly selected indicator has been found to be sufficiently accurate. The suitability of different indicators in the titrations of alkaloids has been considered by McGill (*J. Amer. Chem. Soc.*, 1922, **44**, 2156). In a number of cases the alkaloid solutions were also analysed by conductometric titration with silicotungstic acid (Lamberst and Foster, *Proc. Roy. Soc.*, 1932, **A**, 134, 246). The two sets of data agreed within 1 to 1.5%. Estimation by silicotungstic acid, though accurate, has certain drawbacks. The crystals easily lose water of crystallisation and need recrystallisation before use. Further, the solution has to be standardised before each determination. Estimation by direct titration with suitable indicators, was, therefore, found more convenient and has been generally used in the present experiments. The estimations of caffeine and piperine solutions were carried out by careful evaporation and direct weighing.

Preliminary experiments showed that 90% of the adsorption took place rapidly within the first 24 hours. After this the system continued to change very slowly and complete equilibrium was not established even after several weeks. To determine the exact equilibrium time, 100 c.c. each of 7 alkaloid solutions were kept in well stoppered bottles with 5 g. of gel and changes in the concentrations of the alkaloid solutions were followed over a period of 75 days. The results are given in Table I.

TABLE I.

Rate of adsorption of alkaloids by silica gel.

| No of days. | Changes in concentration titre against $N/100$ HCl | | | | | | | | |
|--------------|--|-------|-------|------|------|------|------|------|------|
| | 0 | 3 | 6 | 10 | 15 | 20 | 40 | 60 | 70 |
| Morphine | 7.70 | 6.20 | 5.90 | 5.70 | 5.40 | 5.30 | 5.30 | — | — |
| Nicotine | 13.70 | 10.90 | 10.90 | — | — | — | — | — | — |
| Quinine | 6.95 | 6.00 | 5.70 | 5.60 | 5.50 | 5.40 | 5.40 | — | — |
| Quinidine | 7.55 | 6.35 | 6.05 | 5.90 | 5.85 | 5.80 | 5.80 | — | — |
| Cinchonidine | 8.15 | 6.85 | 6.75 | 6.60 | 6.50 | 6.40 | 5.40 | — | — |
| Brucine | 5.20 | 3.60 | 3.30 | 3.00 | 2.80 | 2.60 | 2.30 | 2.10 | 2.10 |
| Strychnine | 4.10 | 2.40 | 2.10 | 1.90 | 1.75 | 1.70 | 1.60 | 1.60 | — |

From Table I complete equilibrium appears to be established in most cases only after 20 days, except in the case of nicotine where equilibrium was established within 3 days.

Adsorption from solutions is generally considered to be rapid, equilibrium being established in a few hours or a few days. In the case of brucine in the present experiments, the equilibrium was not complete till after 60 days. Such a long equilibrium time raises the question as to whether the changes in the titration values are really due to slow attainment of equilibrium or are due to some slow chemical change occurring in the system. It is well known that alcohol undergoes dehydration or oxidation in the vapour phase in presence of a proper catalyst. If silica gel were playing a similar role, alcohol, even in the liquid phase, on prolonged contact with the gel, might undergo chemical changes. To test the point a blank experiment was performed. After standing in contact with the gel for about two weeks, the alcohol gave no tests for either ethylene or aldehydes, but had developed minute traces of acid. The possibility of any chemical change in the alcohol itself thus seems remote. One must, therefore, conclude that the attainment of equilibrium in these adsorption experiments is really an extremely slow process.

A set of adsorption values for alcoholic solutions of different alkaloids is given in Table II.

TABLE II.

25 C.c. of solution treated with 5 g. of gel in each case.

| Alkaloid | Initial conc. (g/100 c.c.) | Initial titre (c.c.) | Final titre (c.c.) | Adsorption. | Alkaloid | Initial conc (g/100 c.c.) | Initial titre (c.c.) | Final titre (c.c.) | Adsorption. |
|-----------|----------------------------|----------------------|--------------------|-------------|--------------|---------------------------|----------------------|--------------------|-------------|
| Morphine | 0.5 g | 23.7 | 8.4 | 63.7% | Cinchonidine | 0.5 g | 25.0 | 9.2 | 63.2% |
| Nicotine | „ | 42.0 | 19.0 | 78.5 | Brucine | „ | 16.0 | 2.7 | 83.1 |
| Quinine | „ | 21.2 | 10.8 | 49.0 | Strychnine | 0.4 | 14.0 | 1.3 | 80.6 |
| Quinidine | „ | 23.3 | 8.9 | 61.8 | Caffeine. | 0.25 | — | — | 20.8 |
| | | | | | Piperine | 0.25 | — | — | 2.4 |

Table II indicates that positive adsorption is obtained in every case except in that of piperine, where the solution after treatment with the gel was slightly more concentrated and thus established negative adsorption. As is well known silica gel can adsorb considerable quantities of alcohol vapour (*cf.* Lambert and Foster, at saturation 0.218 c.c. of alcohol are adsorbed per g. of the gel). If the same amount of alcohol be removed by preferential adsorption by silica gel from the alcoholic solution of piperine, it would introduce an increase in concentration of 3.8%. This is of the same order as actually found with the piperine solution. The observed negative adsorption is, therefore, simply due to the preferential adsorption of the alcohol from the solution. That piperine itself is not adsorbed was also found by washing the gel free from adhering solution and then treating the dry gel with concentrated acid when no colour or stain was developed. Incidentally it might be mentioned that the same amount of alcohol must be preferentially adsorbed by the gel in the case of the other alkaloid solutions also. The amount, however, is small and would not materially alter the amounts of adsorption.

To study the effect of concentration on the adsorption process, adsorption isotherms have been determined and the results are given in the following tables. The concentration terms in the tables refer to the amounts in g. mols present in 25 c.c. of the solution. x/m represents the number of mols ($\times 10^5$) of alkaloid adsorbed per g. of gel.

TABLE III.

25 C.c. of morphine solution treated with 4 g. of gel.

| Initial conc | Equil. conc. | Amount adsorbed | x/m . | log C. | log x/m . |
|-----------------------|-----------------------|-----------------------|---------|--------|-------------|
| 8.77×10^{-5} | 2.04×10^{-5} | 6.73×10^{-5} | 1.68 | 0.3096 | 0.2253 |
| 17.54 | 6.12 | 11.42 | 2.86 | 0.7868 | 0.4564 |
| 26.31 | 11.42 | 14.89 | 3.72 | 1.9577 | 0.5705 |
| 35.08 | 16.52 | 18.56 | 4.64 | 1.2186 | 0.6665 |
| 43.85 | 22.23 | 21.62 | 5.41 | 1.3470 | 0.7332 |

TABLE IV.

25 C.c. of nicotine solution treated with 3 g. of gel.

| Initial conc | Equil. conc | Amount adsorbed | x/m . | log C. | log x/m . |
|------------------------|-----------------------|------------------------|---------|--------|-------------|
| 15.43×10^{-5} | 5.43×10^{-5} | 10.00×10^{-5} | 3.33 | 0.7340 | 0.5224 |
| 30.86 | 12.01 | 18.85 | 6.28 | 1.0795 | 0.7980 |
| 46.29 | 19.41 | 26.88 | 8.96 | 1.2880 | 0.9523 |
| 61.72 | 26.65 | 35.07 | 11.69 | 1.4257 | 1.0679 |
| 77.15 | 34.38 | 42.77 | 14.26 | 1.5363 | 1.1541 |

TABLE V.

25 C.c. of quinine solution treated with 5 g. of gel.

| Initial conc. | Equil. conc. | Amount adsorbed. | x/m . | log C. | log x/m . |
|-----------------------|-----------------------|-----------------------|---------|--------|-------------|
| 6.61×10^{-5} | 2.55×10^{-5} | 4.06×10^{-5} | 0.82 | 0.4065 | -0.0862 |
| 13.22 | 5.70 | 7.52 | 1.50 | 0.7559 | 0.1761 |
| 19.83 | 9.36 | 10.53 | 2.11 | 0.9685 | 0.3243 |
| 26.44 | 12.90 | 13.54 | 2.71 | 1.1106 | 0.4330 |
| 33.05 | 16.80 | 16.25 | 3.25 | 1.2253 | 0.5119 |

TABLE VI.

25 C.c. of quinine solution treated with 3 g. of gel.

| Initial conc. | Equil. conc. | Amount adsorbed. | x/m . | log C. | log x/m . |
|-----------------------|-----------------------|-----------------------|---------|--------|-------------|
| 7.72×10^{-5} | 4.75×10^{-5} | 2.97×10^{-5} | 0.99 | 0.6767 | -0.0004 |
| 15.43 | 9.84 | 5.59 | 1.86 | 0.9930 | 0.2695 |
| 23.15 | 14.76 | 8.39 | 2.80 | 1.1690 | 0.4472 |
| 30.86 | 19.68 | 11.18 | 3.73 | 1.2940 | 0.5717 |
| 38.58 | 24.92 | 13.66 | 4.55 | 1.3966 | 0.6580 |

TABLE VII.

25 C.c. of cinchonidine solution treated with 3 g. of gel.

| Initial conc. | Equil. conc. | Amount adsorbed. | x/m . | $\log C$. | $\log x/m$. |
|-----------------------|-----------------------|-----------------------|---------|------------|--------------|
| 8.52×10^{-5} | 4.84×10^{-5} | 3.68×10^{-5} | 1.23 | 0.6848 | 0.0899 |
| 17.04 | 9.85 | 7.19 | 2.42 | 0.9914 | 0.3800 |
| 25.56 | 15.03 | 10.53 | 3.51 | 1.1769 | 0.5433 |
| 34.08 | 20.54 | 13.54 | 4.51 | 1.3126 | 0.6542 |
| 42.60 | 26.22 | 16.38 | 5.46 | 1.4186 | 0.7372 |

TABLE VIII.

25 C.c. of brucine solution treated with 5 g. of gel.

| Initial conc. | Equil. conc. | Amount adsorbed. | x/m . | $\log C$ | $\log x/m$ |
|-----------------------|-----------------------|-----------------------|---------|----------|------------|
| 5.36×10^{-5} | 0.57×10^{-5} | 4.79×10^{-5} | 0.96 | -0.2441 | -0.0177 |
| 10.73 | 1.32 | 9.41 | 1.88 | 0.1206 | 0.2742 |
| 16.09 | 2.30 | 13.79 | 2.76 | 0.3607 | 0.4404 |
| 21.46 | 3.23 | 18.23 | 3.65 | 0.5092 | 0.5623 |
| 26.82 | 4.56 | 22.26 | 4.45 | 0.6590 | 0.6484 |

TABLE IX.

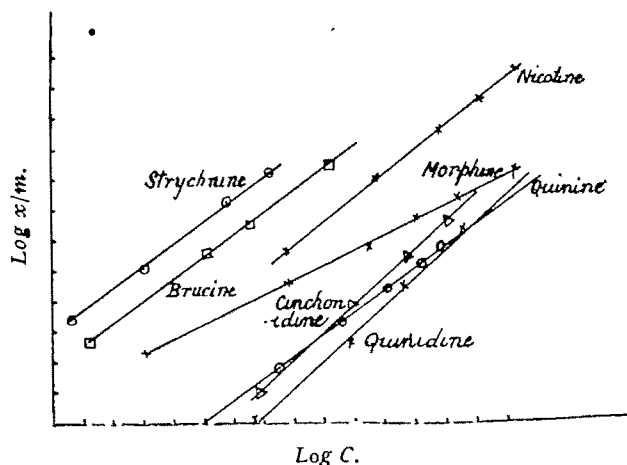
25 C.c. of strychnine solution treated with 5 g. of gel.

| Initial conc. | Equil. conc. | Amount adsorbed | x/m | $\log C$. | $\log x/m$. |
|-----------------------|------------------------|-----------------------|-------|------------|--------------|
| 6.00×10^{-5} | 0.429×10^{-5} | 5.57×10^{-5} | 1.11 | -0.3675 | 0.0453 |
| 12.00 | 1.144 | 10.86 | 2.17 | 0.0584 | 0.3365 |
| 18.00 | 2.002 | 16.00 | 3.20 | 0.3014 | 0.5031 |
| 24.00 | 2.860 | 21.14 | 4.30 | 0.4564 | 0.6335 |
| 30.00 | 3.718 | 26.28 | 5.26 | 0.5705 | 0.7210 |

The adsorption isotherms are shown in Fig. 1. The amount of adsorption has been reckoned in terms of g.mols of the alkaloid per g. of the gel. The concentration values used in plotting the isotherms represent equilibrium concentrations. As will be seen from the figure, the plot of $\log x/m$ against $\log C$ is generally a straight line. The adsorption of the alkaloids thus follows the Freundlich adsorption equation.

An examination of the figure further shows that the adsorption isotherms for brucine and strychnine run parallel and close to one another. These

FIG. 1.



two alkaloids are similar in constitution and differ from one another in respect of two methoxy groups only. So far as this pair of alkaloids is concerned, it would appear that compounds similar in constitution have comparable adsorption. A parallelism between constitution and adsorption is also seen in the case of the cinchona alkaloids. The adsorption isotherms of cinchonidine, quinidine and quinine form a cluster which are close to one another. The isotherms of quinidine and cinchonidine are parallel to one another, the values for quinine lying practically intermediate between these isotherms. Bearing in mind the fact that the cinchona alkaloids are difficult to obtain in an absolutely pure state, the three adsorption isotherms may be considered and sufficiently close to one another to justify the conclusion that compounds allied in constitution have similar adsorption.

A comparison of the tables given above shows that brucine, strychnine and nicotine are adsorbed the most from solutions. It is interesting to note that in respect of physiological action, the above three are the most poisonous amongst all the alkaloids studied in these experiments. Morphine has shown a distinctly lower adsorption. Its pharmacopoeic dose is between 6.39 mg. compared to 1.4 mg. for strychnine. Piperine which has no positive adsorption at all is not ordinarily a poison. There is thus a definite indication that the alkaloids which act physiologically as powerful poisons are very largely adsorbed. The point, however, should not be stretched too far for obvious reasons.

TABLE X.

| Alkaloid | Initial titre. | Final titre. | | | | $\left(\frac{x/m \text{ at } 45^\circ}{x/m \text{ at } 35^\circ}\right) \left(\frac{x/m \text{ at } 40^\circ}{x/m \text{ at } 30^\circ}\right)$ | |
|--------------|-------------------|--------------|------|------|------|---|-------|
| | | 30°. | 35°. | 40°. | 45°. | | |
| Nicotine | 23.7 | 15.7 | 18.0 | 19.8 | 20.6 | 0.544 | 0.488 |
| Quinine | 13.9 | 9.1 | 10.5 | 11.3 | 11.8 | 0.618 | 0.542 |
| Brucine | 10.4 | 2.5 | 3.3 | 4.2 | 4.9 | 0.775 | 0.785 |
| Morphine | 15.4 | 8.0 | 9.1 | 10.2 | 11.1 | 0.683 | 0.703 |
| Cinchonidine | 16.7 | 10.4 | 10.9 | 11.6 | 12.0 | 0.825 | 0.809 |
| Quinidine | 15.0 | 10.1 | 10.7 | 11.4 | 12.0 | 0.659 | 0.325 |
| Strychnine | 8.4 | 1.9 | 2.4 | 3.0 | 3.6 | 0.800 | 0.831 |

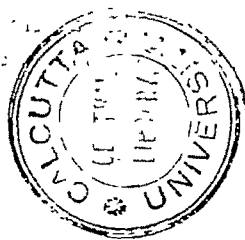
The effect of temperature on the adsorption processes has also been studied. Experiments were performed at 30°, 35°, 40°, and 45° and the results are given in Table X.

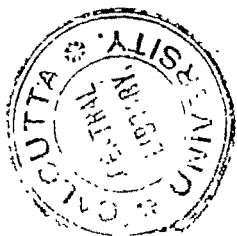
The temperature coefficients are given in the last two columns of the table. As will be seen from the values a ten degree rise in temperature reduces the amount of adsorption by 30 to 50%.

Further experiments are in progress.

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Received July 17, 1942





STUDIES IN GLASS SYSTEMS: X-RAY ANALYSIS OF NaCl DISSOLVED IN B₂O₃-GLASS.

BY SUBODH KUMAR MAJUMDAR AND RANENDRA MOHAN PALIT.

The lattice distance of sodium chloride dissolved in boric oxide glass has been measured by Debye-Scherrer method, and is found to be 9.088\AA , which represents more than 60% increase over the normal value. A theoretical explanation of the increase is given.

The properties of polar crystals in the crystalline state, in aqueous solution and in the gaseous condition have been investigated by different workers of the Fajans school (Fajans, *Z. physikal. Chem.*, 1934, **B**, 24, 103; *Z. Elektrochem.*, 1928, **34**, 503; Wulff and Heigl, *Z. Kristallographie*, 1931, **77**, 85; Wulff and Schaller, *ibid.*, 1934, **A**, 87, 53). Wulff and Majumdar (*Z. physikal. Chem.*, 1936, **B**, 31, 319) studied the mole refraction of the system $x\text{Na}_2\text{O}$, $y\text{B}_2\text{O}_3$ and found that $\text{Na}_2\text{B}_4\text{O}_7$ in solid solution in B_2O_3 -glass is markedly deformed, the extent of deformation produced being of a much greater magnitude than in the corresponding aqueous solution. Zachariasen (*J. Amer. Chem. Soc.*, 1932, **54**, 3841) also studied similar systems and concluded that polar crystals in solid solution are present in the molecular as opposed to the ionic state in glass systems. Majumdar and Sarma (*J. Indian Chem. Soc.*, 1942, **14**, 241) have studied the systems $\text{XCl}-\text{B}_2\text{O}_3$ at different concentrations and found that the deformation rule of Fajans holds good *qualitatively* in the case of solid solution of alkali halides in boric oxide glass, with the difference that the extent of deformation with cations of small diameter is much greater in glass than in aqueous solution or in crystal. Biltz, Weibke and Schraeder (Träger, *Z. anorg. und allg. Chem.*, 1937, **234**, 253) on the other hand from a study of the data of previous workers, hold that the mole-refraction of simple glasses can be explained as equal to the sum of the refractions of the constituent oxides. Kordes (*Z. anorg. und allg. Chem.*, 1939, **241**, 1, 418) on the other hand disputes this idea.

Biltz's contention may be true in the case of pure glasses; Majumdar and Sarma (*loc. cit.*) have proved that in the case of solid solutions of alkali halides in glass such additivity does not hold good, except with cations of large ionic diameter like Cs^+ , which is in complete harmony with the postulates of Fajans (Fajans and Joos, *Z. Physik*, 1924, **23**, 1). It was therefore thought advisable to study the changes in the lattice distance of alkali salts, if any, caused by dissolving them in B_2O_3 -glass.

EXPERIMENTAL.

Preparation of the Samples.—Specially purified boric acid was dehydrated, first in a steam chamber for several hours in thin layers and finally in a vacuum desiccator until a portion dissolved in absolute alcohol did not give coloration with anhydrous copper sulphate. It was mixed with dry and pure sodium chloride in varying proportions and heated in a platinum crucible to $900^\circ - 1000^\circ$ in an electric furnace for several hours until a homogeneous melt was obtained. The crucible was chilled and the solid taken out.

Analysis of the Samples.—A definite weight of the glass was taken in a weighed platinum crucible and treated repeatedly with a mixture of hydrofluoric and sulphuric acids and heated. The residue was weighed as sulphate. A second portion was dissolved in water and chlorine estimated volumetrically by a semi-micro method. In this way the stoichiometric ratio $\text{Na}:\text{Cl}$ was determined. It was found that inspite of the precautions taken in the dehydration of the materials a certain amount of $\text{Na}_2\text{B}_4\text{O}_7$ had been formed. But a considerable amount of NaCl remained dissolved in B_2O_3 .

X-Ray Analysis.—Powder photographs were taken of the samples by the Debye-Scherrer method. The X-rays were produced by a demountable type of X-ray tube designed by Hadding. It consisted of a metal cylinder with a conical mouth at one end; to this a metal cone provided with a water circulating cooling device was fitted by means of Ramsay grease. This formed the anti-cathode. The cathode consisted of an aluminium disc with a concave surface from which the electron stream was focussed on the target below. A porcelain insulator insulated the high potential cathode from the metal parts. X-rays generated from the metal target left the tube through the openings covered with thin aluminium foils of thickness 0.0015 cm. fixed against the window faces by means of grease and tightened with the help of washers fitted with screws. Pure electrolytic copper was used as the anti-cathode and copper K -radiations were used throughout, $K\alpha_1$, $K\alpha_2$ and $K\beta$ being 1.537 Å, 1.541 Å and 1.389 Å respectively: $K\alpha$ was taken as the mean of $K\alpha_1$ and $K\alpha_2$ and equal to 1.539 Å.

The X-ray tube was evacuated to about 10^{-5} to 10^{-4} mm. pressure. This was secured by a two stage mercury pump (Leybold) backed by a Cenco rotary oil pump. The transformer, which was the source of high tension, was directly connected with the cathode without any rectifying device as the tube was self-rectifying. The tube was operated at 35-40 K.V. and 5-6 milliampere current. The voltage applied to the primary of the transformer was regulated by means of an auto-transformer.

The X-ray beam coming out was made parallel by causing it to pass it through a series of slits. The latter was held in proper position by means of brass rings attached to metal base provided with levelling screws.

The film holder, which could slide against a groove in the metal base perpendicular to it, consisted of a rectangular brass frame with a brass lid at the back. The front portion was screened with a piece of black paper which could transmit X-rays. The plate holder could be fixed at any desired distance from the slit cap.

Pure NaCl crystal



FIG. 1

Pure $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystal

FIG. 2

NaCl (8.21%) dissolved in B_2O_3 

FIG. 3

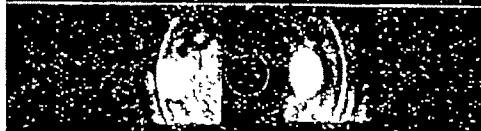
NaCl (7.98%) dissolved in B_2O_3 

FIG. 4

The solid specimen under examination was first carefully ground in an agate mortar. A piece of zigzag paper was gummed to the slit cap by secotine and the fine powder was rubbed against the central part for exposure to the X-rays. The optimum thickness of the film would be given by the formula $t = 1/\mu$, μ is the mass absorption coefficient. By trial, however, the proper thickness was secured. The powdering was done in such a way that particles of the size 10^{-3} to 10^{-5} cm. diam. could be obtained.

The films were exposed to the X-rays for 12 hours and then developed. Figures 1, 2, 3, 4 give respectively the results of pure NaCl crystal, pure $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystals (without melting), and two samples of $\text{NaCl}-\text{B}_2\text{O}_3$ glass.

B_2O_3 -glass formed by melting and solidifying pure boric acid did not give any lines testifying that it formed a true glass. Crystals of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ on the other hand gave lines as shown in Fig. 2.

DISCUSSION.

It was expected that absolutely anhydrous B_2O_3 and NaCl would not react with each other even at high temperature. Chemical analysis of the solidified glass on the other hand indicated that a certain amount of borate had been formed although a considerable amount of NaCl remained in solid solution in B_2O_3 -glass. The percentages of NaCl shown in Figs. 3 and 4 have been calculated after allowing for the borate formed.

It is well known that the spacing of a crystal in the powder photography method first enunciated by Debye and Scherer (*Physikal Z.*, 1916, 17, 277) and later by Hull (*Phys. Rev.*, 1917, 10, 661) may be calculated from the following formula

$$\frac{4a_0^2 \sin^2 \theta_n}{\lambda^2} = (h^2 + k^2 + l^2) n^2 \quad \dots (i)$$

where a_0 is the spacing of the plane (h, k, l) from which cumulative reflection of X-rays takes place, θ_n is the angle of the cone where the reflection is of the n th order and λ is the wave-length of the X-ray employed. The semi-circumference of the camera employed was 12.9 cm., from which the radius works out to be 4.1092 cm. Hence if x be the distance of a pair of similar lines (actually the mean of the distances taken at each extremity of the lines), then θ , the angle of the cone subtended is given by

$$\theta = \frac{x}{4r} \times 57.3 \text{ degrees.} \quad \dots (ii)$$

In the following tables x represents the distance in cm. between a pair of similar lines, w stands for weak lines, s for sharp lines, and v indicates very.

TABLE IA.

Analysis of photograph pure NaCl (Fig. 1).

| | | | | | | | |
|--------|------|-----|------|------|------|------|-------|
| x | 4.21 | 4.7 | 6.04 | 6.75 | 8.35 | 9.76 | 11.05 |
| Nature | w | s | w | s | w | v.w | v.w |

TABLE IB.

Pure $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystals (Fig. 2).

| | | | | | | | | |
|--------|-------|------|------|------|------|------|-------|-------|
| x | 1.515 | 1.9 | 2.48 | 2.92 | 3.44 | 3.72 | 4.51 | 4.82 |
| Nature | w | w | w | s | w | s | s | v.w |
| x | 5.64 | 6.08 | 6.72 | 7.52 | 8.3 | 8.74 | 9.12 | 9.42 |
| Nature | w | s | s | s | v.w | v.w | v.v.w | v.v.w |

TABLE IC.

NaCl (8.21%) dissolved in B_2O_3 (Fig. 3).

| | | | | | | | | | | |
|--------|-------|------|-------|------|-------|------|-------|-------|-------|------|
| x | 1.515 | 1.87 | 2.28 | 2.51 | 2.755 | 3.28 | 3.446 | 3.685 | 4.088 | 4.54 |
| Nature | w | v.w | s | v.w | s | w | v.w | s | v.s | s |
| x | 5.08 | 5.46 | 5.952 | 6.48 | 6.91 | 7.13 | 7.6 | | | |
| Nature | s | w | s | w | v.w | v.w | v.v.w | | | |

TABLE ID.

NaCl (7.98%) dissolved in B₂O₃-glass (Fig. 4).

| | | | | | | | | | |
|--------|-------|------|------|------|-------|-------|------|-------|--------|
| x | 1'515 | 1'84 | 2'28 | 2'51 | 2'755 | 2'906 | 3'28 | 3'446 | 3'685 |
| Nature | w | v.w. | s | v.w. | s | s | w | v.w. | s |
| x | 4'11 | 4'52 | 5'08 | 5'46 | 5'95 | 6'52 | 6'91 | 7'13 | 7'6 |
| Nature | v.s | s | s | w | s | w | v.w. | v.w. | v.v.w. |

It is clear from Tables IC and ID that the lines corresponding to Figs. 3 and 4 are almost identical.

For the purpose of calculation of the spacing the following trial method was adopted. The distance, x , between any pair of lines was measured and from equation (ii) the value of θ calculated. Sine of this angle was divided separately by $\sqrt{1}$, corresponding to (1,0,0) plane, $\sqrt{2}$, corresponding to (1,1,0) plane, $\sqrt{3}$, corresponding to (1,1,1) plane, $\sqrt{4}$, corresponding to (2,0,0) plane and so on and the values tabulated. As is compatible with theory, constant values will be obtained for NaCl corresponding to $\frac{\sin\theta}{\sqrt{4}}$, $\frac{\sin\theta}{\sqrt{8}}$, and so on. The mean of these values is taken. For NaCl, this constant works out for K_β (1.389 Å) to be 0.12645 and for K_α (1.539 Å) at 0.1409. From (i)

$$a_0 = \frac{\sqrt{(h^2 + k^2 + l^2)} \cdot \lambda}{\sin\theta} \quad \text{for the first order of reflection}$$

$$= \frac{\lambda}{2 \cdot \frac{\sin\theta}{\sqrt{(h^2 + k^2 + l^2)}}}$$

Hence a_0 for NaCl with K_β works out

$$\frac{1.389 \times 10^{-8}}{2 \times 0.1264} = 5.495 \text{ Å}$$

and with K_α

$$\frac{1.539 \times 10^{-8}}{2 \times 0.1409} = 5.465 \text{ Å, the mean value being } 5.479 \text{ Å, [which}$$

is in fairly good agreement with the standard value 5.628 Å (Bragg, *Proc. Roy. Soc.*, 1913, **89A**, 246).

Considering the photographs in Figs. 3 and 4, we find in these some lines (e.g. $x=1.515$, 2.48, 2.9, 3.44, etc.) due to sodium borate. Eliminating these by comparing Figs 3 & 4 with Fig. 2, we take the reflections corresponding to $\frac{\sin\theta}{\sqrt{4}}$, $\frac{\sin\theta}{\sqrt{8}}$, $\frac{\sin\theta}{\sqrt{12}}$, and so on. These must have originated from NaCl dissolved in the glass due to reflections from the planes (2,0,0), (2,2,0), (2,2,2), etc. The mean value of $\frac{\sin\theta}{\sqrt{(h^2 + k^2 + l^2)}}$ for K_β is found to be 0.0767 and that for K_α 0.0944.

Hence a_0 for NaCl dissolved in the glass corresponding to K_α

$$= \frac{1.539 \times 10^{-8}}{2 \times 0.0944} = 9.120 \text{ Å}$$

and the value corresponding to K_β

$$= \frac{1.389 \times 10^{-8}}{2 \times 0.0767} = 9.057 \text{ Å, the mean value being } 9.088 \text{ Å.}$$

The calculations of the other sample corresponding to Fig. 4 are not given in detail but it gives rise to almost identical value of spacing. This increase of about 60% of the lattice distance of NaCl when dissolved in a glass is very interesting and may be discussed from the theoretical standpoint.

It is well known that NaCl crystal is regarded as a polar lattice, i.e. sodium and chlorine are present in the ionic condition in the lattice forming what is called a face-centred cubical lattice. Born and Lande (*Verhandl. deuts. physikal. Gesellsch.* 1918, 20, 210) were the first to postulate the lattice theory of polar crystals. They enunciated the existence of two types of forces, electrostatic due to the mutual attraction and repulsion of the charges and a repulsive force between opposite charges operating within a *very short* distance. The potential energy of an isolated ion was calculated by considering the work that has to be expended in order to bring a similar ion from infinity to that point. These forces, electrostatic or otherwise, must be considered in three dimensions, along each of which there will be a divergent series involving a function of the spacing in the denominator, alternately positive and negative. By an ingenious method these authors have evaluated the series so that u may be represented by the formula

$$u = A.e.^2/a_0 + B/a_0^n,$$

where A is a numerical constant called the Madelung constant and B , a second constant due to the repulsive force. The value of n for the repulsive forces worked out to be 9 according to Born but a much lower value of the order of 5 was obtained by other workers.

The original theory of Born has undergone considerable modification. London (*Naturwiss.*, 1929, 17, 516), Lennard Jones and Taylor (*Proc. Roy. Soc.*, 1925, 109, A, 476; *Trans. Faraday Soc.*, 1937, 33, 8), Slater and Kirwood (*Phys. Rev.*, 1924, 23, 488; Born and Mayer (*Z. Physik*, 1932, 75, 1), Pauling (*Z. Krist.*, 1928, 67, 377) and others have introduced important modifications to the simple theory of Born. For example in the original theory the effect of the Van der Waals forces was neglected. But quite satisfactory agreement between experimental value of lattice energy of alkali halides and that calculated on the basis of the Born-Haber cycle has been obtained in the case of alkali halides. And it was only in the case of the II-group metals that the inadequacy of the treatment was recognised.

In their calculation of the potential of an isolated ion, Born and Lande have assumed the dielectric constant of the medium to be unity implying that there is no dielectric intervening the ions in the lattice. If on the other hand a dielectric medium intervenes, as in the present case, the potential of the ions will be altered as the electrostatic forces of attraction between oppositely charged ions will be diminished, the dielectric constant factor occurring in the denominator. For a lattice of the NaCl type, the potential is given by

$$u = -\frac{1.746 \cdot N_L \cdot e^2}{a_0} \quad \text{where } N_L = \text{Avogadro No. and } 1.746 = \text{Madelung const.} = A.$$

Taking the dielectric constant into consideration, the modified formula for the potential will be

$$u = A.e.^2/D.a_0 + B/a_0^n.$$

The dielectric constant of B_2O_3 -glass is known to be 3.5 (Thomas, *J. Phys. Chem.*, 1931, 35, 2109) and those of different borates lie between 6.44 and 7.50 (Landolt-Börnstein Tabellen, 1923, II, 1033). The effect of the dielectric on the repulsive forces, as well as on the Van der Waals forces will be comparatively small. The total effect of introducing an intervening medium of dielectric constant higher than unity will be therefore to decrease the Coulomb forces of attraction.

The direct outcome of this will be that the spacing will be increased, if the repulsive forces are not affected or at any rate not affected to the same extent as the electrostatic forces. There are theoretical reasons to believe that these short distance forces will not be affected to the same extent as the Coulomb forces by the new dielectric. If they were completely unaffected then the lattice distance would be increased much more than in the present case. But since the actual increase is about 66%, the repulsive forces must also be affected by the higher dielectric constant to a certain extent. And this is also true of the Van der Waals forces probably to a much smaller extent. Hence the deciding factor in the spacing of the lattice of a polar crystal dissolved in a medium is the dielectric constant of the medium. It would be interesting to compare the spacings of the same crystal dissolved in media of different dielectric constants, and experiments are in progress in this direction.

It may be suggested that the shifted lines are due entirely to different compounds. That some compounds are actually formed is shown by the complexity of the lines (Figs. 3 & 4). As has been pointed out, lines due to $\text{Na}_2\text{B}_4\text{O}_7$ are present both in Figs. 3 & 4, and these have been eliminated by comparison with Fig. 2. It is curious, however, that even after solidification of the fused mass, $\text{Na}_2\text{B}_4\text{O}_7$ should be present in the crystalline state in the solidified glass. This may be compared to the well known phenomenon of devitrification of glass. There is no evidence that a complex compound of chlorine with borates is formed, and moreover the strongest evidence that NaCl is present in the crystalline state dissolved in glass is that sharp lines are obtained from certain planes from which sharp lines emerge from the pure crystal as well.

Our thanks are due to Principal B. M. Sen, Principal, Presidency College, for material help in theoretical discussions and encouragement and to Prof. B. B. Ray, Khaira Professor of Physics, University of Calcutta for kindly permitting us to use his apparatus.

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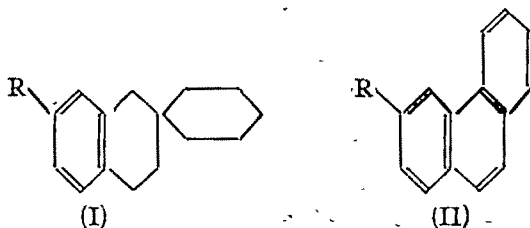
Received September 17, 1942.

STUDIES IN DEHYDROGENATION. PART VII.

BY SURESH CHANDRA SEN-GUPTA.

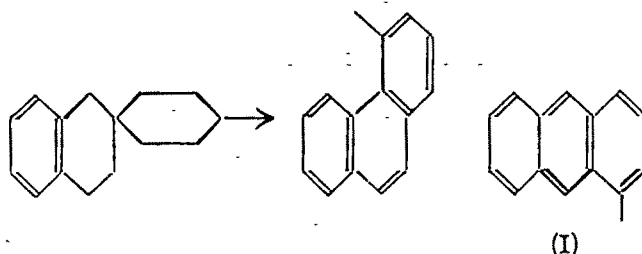
The syntheses and selenium dehydrogenation of tetrahydronaphthalene-2 : 2-spirocyclohexane, 7-methyl- and 7-ethyl-tetrahydronaphthalene-2 : 2-spiro-cyclohexane have been described.

The results obtained by the selenium dehydrogenation of tetrahydronaphthalene-spiro-cyclopentane derivatives had been described in a former communication in this series (*J. Indian Chem. Soc.*, 1939, 16, 350). The author's view explaining the ring transformation that takes place during dehydrogenation had also been advanced there. In the present communication the effect of selenium dehydrogenation on three tetrahydronaphthalene-spiro-cyclohexanes has been studied. The spiro-cyclohexanes synthesised for this purpose are 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane (I, R=H), 7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane (I, R=Me) and 7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane (I, R=Et). All the three spiro-cyclohexanes are found to undergo ring transformation, exactly as in the case of the spiro-cyclopentane compounds (*loc. cit.*) during dehydrogenation with selenium with the formation of fully aromatic hydrocarbons. In all the cases studied here, it is found that along with ring transformation there occurs a loss of one carbon atom during dehydrogenation.

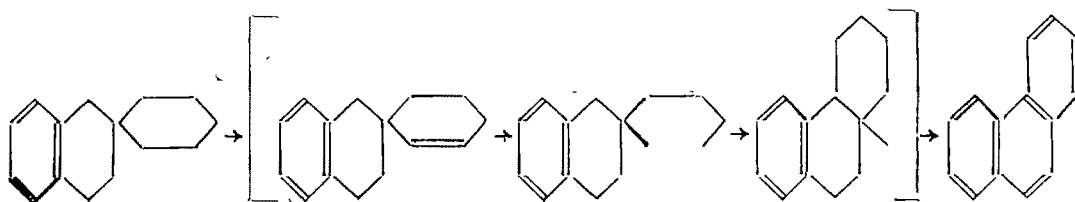


1 : 2 : 3 : 4-Tetrahydronaphthalene-2 : 2-spiro-cyclohexane (I, R=H) gives on dehydrogenation only phenanthrene and no anthracene or methylphenanthrene could be isolated from the dehydrogenation product. By an identical ring transformation and loss of one carbon atom, the spiro-cyclohexanes (I, R=Me) and (I, R=Et) afford 3-methylphenanthrene (II, R=Me) and 3-ethylphenanthrene (II, R=Et) respectively and no anthracene derivative could be detected in the dehydrogenation products.

This result is rather difficult to explain. From analogy with the cyclopentane series discussed in a previous paper (*loc. cit.*), the spiro-cyclohexane ring should be expected to furnish by similar fission and recyclication a methylphenanthrene and a methylanthracene. It is quite

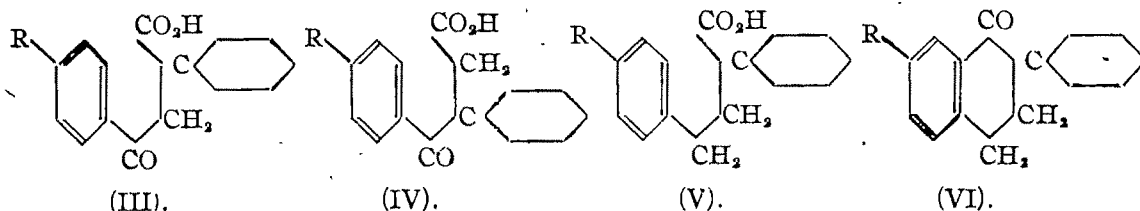


probable, however, that the cyclohexane ring undergoes partial dehydrogenation, fission then takes place with the formation of an intermediate product which by cyclisation and dehydrogenation furnishes phenanthrene according to the following scheme



In the absence of a better explanation this view has been adopted by the author as providing a satisfactory explanation of the curious behaviour of the *cyclohexane-spiro* compounds on dehydrogenation.

The spiro-hydrocarbon (I, R=H) has been synthesised in the following manner. The anhydride of *cyclohexane-1-carboxy-1-acetic* acid is condensed with benzene in presence of anhydrous aluminium chloride, with the formation of a keto-acid which might be either (III, R=H) or (IV, R=H). The same keto-acid is also obtained by the condensation of the acid chloride of methyl *cyclohexane-1-carboxy-1-acetate* (*J. Chem. Soc.*, 1926, 2015) with benzene in presence of aluminium chloride. Reduction of this keto-acid by the Clemmensen method gives an acid which has been proved to be *α-cyclohexane-γ-phenyl* butyric acid (V, R=H), on the ground that the ethyl ester of this acid does not condense with ethyl oxalate in presence of potassium ethoxide. This acid (V, R=H) on cyclisation with 85% sulphuric acid gives the spiro-ketone (VI, R=H), which on reduction with amalgamated zinc and hydrochloric acid gives the spiro-hydrocarbon (I, R=H).



By an extension of this process the spiro-hydrocarbons (I, R=Me and R=Et) have also been synthesised. The anhydride of *cyclohexane-1-carboxy-1-acetic* acid is condensed with toluene and ethylbenzene in presence of anhydrous aluminium chloride giving the keto-acids (III, R=Me) and (III, R=Et) respectively. These keto-acids on reduction by the Clemmensen method give *α-cyclohexane-γ-(p-tolyl)*-butyric acid (V, R=Me) and *α-cyclohexane-γ-(p-tolyl)* phenyl butyric acid (V, R=Et) respectively. The position of the *cyclohexane* ring in the two *γ-aryl*butyric acids has been proved from the observation that the ethyl esters of these two acids do not condense with ethyl oxalate in presence of potassium ethoxide. These two *γ-aryl*butyric acids on cyclisation with 85% sulphuric acid give the two spiro-ketones (VI, R=Me) and (VI, R=Et). On reduction by the Clemmensen method these spiro-ketones give 7-methyl-1:2:3:4-tetrahydronaphthalene-2:2-spiro-*cyclohexane* (I, R=Me) and 7-ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spiro-*cyclohexane* (I, R=Et).

EXPERIMENTAL.

α-cycloHexane-β-benzoylpropionic Acid (III, R=H).—(a) Aluminium chloride (25 g.) was slowly added to an ice-cooled solution of the anhydride of *cyclohexane-1-carboxy-1-acetic* acid (34 g.) in dry benzene (100 c.c.). The mixture was allowed to stand at the room temperature for 12 hours after which it was heated at 60-65° for 3 hours and decomposed with ice and hydrochloric acid. Excess of benzene was removed in steam and the thick oily product was dissolved in dilute sodium carbonate solution, filtered and acidified with hydrochloric acid when the keto-acid separated as a thick oil which slowly became semi-solid. The mass was dissolved in hot glacial acetic acid from which the keto-acid slowly crystallised in colourless plates. On recrystallisation

it had m. p. 117-18°, yield 12 g. (Found: C, 73.2; H, 7.4. $C_{15}H_{18}O_3$ requires C, 73.2; H, 7.3 per cent).

The *semicarbazone*, prepared in methyl alcoholic solution, crystallised from dilute alcohol in needles, m.p. 132-33°. (Found: C, 63.2; H, 7.0. $C_{16}H_{21}O_3N_3$ requires C, 63.4; H, 6.9 per cent).

(b) The acid chloride prepared from 20 g methyl cyclohexane-1-carboxy-1-aceate was mixed with dry benzene (50 c.c.) cooled in ice and aluminium chloride (26 g.) was added to it. The mixture was allowed to stand at the room temperature for 12 hours and was then treated with ice. Excess of benzene was distilled in steam, the residual oil was extracted with ether, washed with dilute sodium carbonate solution, dried with sodium sulphate and ether removed. The keto-ester (8.1 g.) distilled at 165-70°/3 mm. as a thick oil, which readily solidified on cooling. It was crystallised from petroleum ether (b.p. 40-60°) as white needles, m.p. 65-66°. (Found: C, 73.5; H, 7.9. $C_{16}H_{20}O_3$ requires C, 73.8; H, 7.7 per cent). It was hydrolysed with alcoholic potash and the resulting keto-acid was crystallised from acetic acid as plates, m.p. 117-18°.

aa-cycloHexane-γ-phenylbutyric Acid (V, R=H).—*aa-Cyclohexane-β-benzoyl-propionic acid* (8 g.), amalgamated zinc (50 g.) and concentrated hydrochloric acid (50 c.c.) were boiled for 24 hours. The reduced product was extracted with ether, ether removed and the residue was dissolved in sodium carbonate solution. The filtered solution was acidified with hydrochloric acid and the separated solid acid collected, dried and crystallised from petroleum ether (b.p. 40-60°) in flakes, m.p. 93°, yield 5 g. (Found: C, 77.4; H, 8.6. $C_{16}H_{20}O_2$ requires C, 77.6; H, 8.6 per cent).

The *anilide* was crystallised from alcohol in needles, m.p. 130-31°. (Found: C, 82.2; H, 8.1. $C_{21}H_{23}ON$ requires C, 82.1; H, 8.1 per cent).

The *ethyl ester* was prepared by the action of ethyl alcoholic hydrogen chloride. It is a thin colourless oil, b.p. 111-12°/5 mm. (Found: C, 78.3; H, 9.3. $C_{17}H_{24}O_2$ requires C, 78.5; H, 9.2 per cent).

1-Keto-1: 2: 3: 4-tetrahydronaphthalene-2: 2-spiro-cyclohexane (VI, R=H).—*aa cyclo-Hexane-γ-phenylbutyric acid* (6.5 g.), concentrated sulphuric acid (19.5 c.c.) and water (6.5 c.c.) were heated on a steam-bath for 1½ hours with stirring. The mixture was poured into ice, extracted with ether; the ether extract washed with dilute ammonia and water, dried with sodium sulphate and distilled. It is a colourless oil possessing a characteristic odour, b.p. 145°/3 mm., yield 3.7 g, d_4^{20} , 1.07224; n_D^{20} , 1.56435; $[R_L]_D = 64.9$. (Found: C, 83.9; H, 8.5. $C_{18}H_{18}O$ requires C, 84.1; H, 8.4 per cent).

The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 187-188°. (Found: C, 70.7; H, 7.9. $C_{18}H_{21}ON_3$ requires C, 70.8; H, 7.7 per cent).

1: 2: 3: 4-Tetrahydronaphthalene-2: 2-spiro-cyclohexane (I, R=H).—The foregoing spiro-ketone (3.7 g.) was boiled with hydrochloric acid (20 c.c.) and amalgamated zinc (20 g.) for 24 hours. The product was extracted with ether, the ether extract washed, dried and distilled. It is a colourless liquid, b.p. 115-17°/3 mm., yield 2.5 g. d_4^{20} , 0.98886; n_D^{20} , 1.54314, $[R_L]_D = 63.76$ (Calc., 63.47). (Found: C, 89.8; H, 10.3. $C_{18}H_{20}$ requires C, 90.0; H, 10.0 per cent).

Selenium dehydrogenation of the spiro hydrocarbon (I, R=H).—The spiro-hydrocarbon (2.3 g.) was heated with powdered selenium in a metal-bath at 280-300° for 6 hours and at 340-50° for 24 hours. The product was thoroughly extracted with ether, solvent distilled off and the residual oil was distilled over sodium under reduced pressure. The liquid distillate was warmed with picric acid in alcoholic solution and the separated picrate after two crystallisations from alcohol was obtained as yellow needles, m.p. 144° and the mixed m.p. with the picrate of an

authentic sample of phenanthrene was 144° . The hydrocarbon, regenerated from this picrate by distribution between dilute ammonium hydroxide and ether, crystallised from alcohol in flakes m.p. 99° . The mixed m.p. with an authentic sample of phenanthrene was not depressed. (Found : C, 94.4 ; H, 5.6. $C_{14}H_{10}$ requires C, 94.5 ; H, 5.5 per cent).

α-cycloHexane-β-(p-toluoxy) propionic Acid (III, R=Me).—(a) It was prepared from toluene (70 c.c.), anhydride of cyclohexane-1-carboxy-1-acetic acid (25 g.) and aluminium chloride (40 g.), according to the method followed in the preparation of *α-cyclohexane-β* benzoylpropionic acid. It was crystallised from petrol (b.p. $90-100^\circ$) as colourless long prisms, m.p. $129-30^\circ$, yield 27 g. (Found : C, 73.8 ; H, 7.7. $C_{16}H_{20}O_3$ requires C, 73.8 ; H, 7.7 per cent).

The *semicarbazone* crystallised from dilute alcohol in flakes, m.p. 166° . (Found : C, 64.2 ; H, 7.3. $C_{17}H_{23}O_3N_3$ requires C, 64.3 ; H, 7.3 per cent).

(b) The acid chloride prepared from 15 g. of methyl cyclohexane-1-carboxy-1-acetate and dry toluene (50 c.c.) was treated with aluminium chloride (20 g.). The product, a keto-ester, was worked in the usual manner and distilled as a pale yellow liquid at $180-82^\circ/5$ mm. It solidified on stirring with petroleum ether (b.p. $40-50^\circ$). It crystallised from petrol (b.p. $40-60^\circ$) in stout needles, m.p. $65-6^\circ$ (Found : C, 74.5 ; H, 8.1. $C_{17}H_{22}O_3$ requires C, 74.4 ; H, 8.0 per cent). This keto ester on hydrolysis with alcoholic potash gave a keto acid, m.p. $129-30^\circ$, and the mixed m.p. with a sample prepared by method (a) remained unaltered.

α-cycloHexane-γ-p-tolyl-butyric Acid (V, R=Me).—The preceding keto-acid (22 g.) was gently boiled with amalgamated zinc (110 g.) and hydrochloric acid (110 c.c.) for 24 hours. The product was purified as in the case of the acid (V, R=H). It crystallised from petroleum ether (b.p. $40-60^\circ$) in needles, m.p. $99-100^\circ$, yield 14.5 g. (Found : C, 78.0 ; H, 8.9. $C_{18}H_{22}O_2$ requires C, 78.1 ; H, 8.9 per cent).

The *p-toluidide* crystallised from dilute alcohol in needles, m.p. $128-129^\circ$. (Found : C, 82.5 ; H, 8.8. $C_{23}H_{26}ON$ requires C, 82.4 ; H, 8.7 per cent).

The *ethyl ester* was prepared by the action of ethyl alcoholic hydrogen chloride. It is a thin colourless oil, b.p. $115-16^\circ/6$ mm. (Found : C, 78.7 ; H, 9.6. $C_{18}H_{26}O_2$ requires C, 78.9 ; H, 9.5 per cent).

1-Keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane (VI, R=Me).—*α-cycloHexane-γ-(p-tolyl) butyric acid* (10 g.) was cyclised by heating with concentrated sulphuric acid (30 c.c.) and water (10 c.c.) at 100° . It is a colourless oil, b.p. $158-60^\circ/4$ mm, yield 6.8 g. (Found : C, 84.1 ; H, 8.9. $C_{16}H_{20}O$ requires C, 84.2 ; H, 8.8 per cent).

The *oxime* was prepared by heating the spiro-keto compound with hydroxylamine hydrochloride in pyridine solution. It was crystallised from dilute alcohol in needles, m.p. $139-40^\circ$. (Found : C, 79.1 ; H, 8.6. $C_{16}H_{21}ON$ requires C, 79.0 ; H, 8.6 per cent).

7-Methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane (I, R=Me).—The foregoing spiro-ketone (5.6 g.) was reduced by heating with amalgamated zinc (30 g.) and concentrated hydrochloric acid (30 c.c.) for 18 hours. It is a thin oil, b.p. $155-156^\circ/8$ mm, yield 4.4 g. (Found : C, 89.4 ; H, 10.4. $C_{16}H_{22}$ requires C, 89.7 ; H, 10.3 per cent).

Selenium Dehydrogenation of 7-Methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-cyclohexane.—3.5 g. of the spiro-hydrocarbon was heated with selenium (6 g.) in a metal-bath at $280-300^\circ$ for 8 hours and at $340-355^\circ$ for 30 hours. The product was extracted with ether and distilled over sodium under reduced pressure when 1.2 g. of a yellow liquid distillate was obtained. This was treated with alcoholic solution of picric acid and on crystallisation from alcohol the

picrate was obtained as bright yellow needles, m.p. 133-34°. The hydrocarbon was regenerated from the picrate by distribution between ammonium hydroxide and ether. The ether-solution on evaporation gave the solid hydrocarbon, which on crystallisation from methyl alcohol melted at 62°. The picrate, prepared from this hydrocarbon crystallised from alcohol in bright yellow needles, m.p. 137-138°. The mixed m.p. of this hydrocarbon with a sample of 3-methylphenanthrene, prepared by Haworth's method, was 62°. The mixed m.p. of its picrate with that of 3-methylphenanthrene showed no depression of m.p.

α-cycloHexane-β-(p-ethyl)-benzoyl propionic Acid (III, R=Et).—(a) It was prepared from the anhydride of cyclohexane-1-carboxy-1-acetic acid (16.8 g.), ethylbenzene (12 g.), aluminium chloride (26 g.), in carbon disulphide solution (75 c.c.) according to the procedure followed in the case of *α-cyclohexane-β-(p-toluyloyl) propionic acid*. It was crystallised from petrol (b.p. 70-80°) in beautiful flakes, m.p. 117-18°, yield 17.5 g. (Found: C, 74.2; H, 8.1. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.0 per cent).

The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 144°. (Found: C, 65.3; H, 7.6. $C_{18}H_{25}O_3N_2$ requires C, 65.3; H, 7.5 per cent).

(b) The acid chloride prepared from 20 g. of methyl cyclohexane-1-carboxy-1-acetate and 12 g. of ethylbenzene in 75 c.c. carbon disulphide were treated with anhydrous aluminium chloride (26 g.) in cold. The product, a keto-ester, was worked in the usual manner and was distilled as a thick oil at 202-203°/7 mm, yield 15.5 g. (Found: C, 74.8; H, 8.3. $C_{18}H_{24}O_3$ requires C, 75.0; H, 8.3 per cent). The keto ester was hydrolysed with alcoholic potash and the keto-acid, so obtained, was crystallised from petrol (b.p. 70-80°) and had m.p. and mixed m.p. with a sample of the keto-acid prepared by method (a), 117-18°.

α-cycloHexane-γ-(p-ethyl)-phenylbutyric Acid (V, R=Et).—The foregoing keto-acid (18.5 g.) was reduced by heating with amalgamated zinc (100 g.) and concentrated hydrochloric acid (100 c.c.) for 24 hours. The reduced acid was purified by extraction with sodium carbonate and then by distillation at 220-25°/9 mm. The solid distillate was crystallised from petrol (b.p. 70-80°) in prisms, m.p. 87.88°, yield 13.2 g. (Found: C, 78.5; H, 9.2. $C_{17}H_{22}O_2$ requires C, 78.5; H, 9.2 per cent).

The *ethyl ester* was prepared by the action of ethyl alcoholic hydrogen chloride. It is a thin colourless oil, b.p. 104-105°/6 mm, yield 12.8 g. (Found: C, 79.0; H, 9.7. $C_{18}H_{22}O_2$ requires C, 79.1; H, 9.7 per cent).

1-Keto-7-ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spiro-cyclohexane (VI, R=Et).—*α-cycloHexane-γ-(p-ethyl) phenylbutyric acid* (11g.) was cyclised with concentrated sulphuric acid (33 c.c.) and water (11 c.c.) at 100°. The product was a thick colourless liquid, b.p. 195-97°/9 mm, yield 7.5 g. d_4^{25} , 1.0450, n_D , 1.5536, $[R_L]_D = 74.0$ (Calc., 72.7). (Found: C, 84.0; H, 9.2. $C_{17}H_{22}O$ requires C, 84.3; H, 9.2 per cent).

The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 203-204°. (Found: C, 72.3; H, 8.5. $C_{18}H_{25}ON_3$ requires C, 72.2; H, 8.4 per cent).

7-Ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spiro-cyclohexane (I, R=Et).—The foregoing spiro ketone (6 g.) was reduced by the Clemmensen method with amalgamated zinc (30 g.) and concentrated hydrochloric acid (30 c.c.). The product was purified by distillation over sodium and was a colourless liquid, b.p. 168-69°/8 mm, yield 4.8 g. d_4^{25} , 0.972787, n_D , 1.538808, $[R_L]_D = 73.4$, (Calc., 72.7). (Found: C, 89.3; H, 10.4. $C_{17}H_{24}$ requires C, 89.5; H, 10.5 per cent).

Selenium Dehydrogenation of 7-Ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spiro-cyclohexane.—The spiro-hydrocarbon (3 g.) was heated with selenium (4 g.) in a metal-bath at 300-320° for 6 hours and at 340-350° for 24 hours. The product was thoroughly extracted with ether and distilled over sodium. A liquid distillate (0.9 g.) at 165-175°/5 mm. was obtained. It was treated with picric acid in alcoholic solution and the separated picrate after crystallisation from alcohol was obtained as orange needles, m.p. 117-18°. The mixed m.p. with an authentic sample of picrate of 3-ethylpenanthrene, prepared from 3-phenathroyl methyl ketone (Haworth and Mavin, *J. Chem. Soc.*, 1933, 1012), was 117-18°. (Found: C, 60.7; H, 4.0. $C_{32}H_{17}O_7N_3$ requires C, 60.7; H, 3.9 per cent). The picrate was decomposed with ammonia and the regenerated hydrocarbon after distillation over sodium was obtained as colourless oil, which did not solidify. (Found: C, 93.0; H, 6.8. $C_{14}H_{14}$ requires C, 93.2; H, 6.8 per cent).

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ELECTROLYSIS OF MANGANOUS SULPHATE AND SULPHURIC ACID.

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Results are given of a detailed investigation on the electrolysis of manganous sulphate, in the presence of sulphuric acid. Optimum conditions have been worked out for the anodic oxidation of manganous sulphate. The role of the various electrochemical factors, such as the relative proportions of manganous sulphate and sulphuric acid, the temperature, the inter-electrode distance, the current-density at the anode and at the cathode, the current concentration, the duration of electrolysis, the anode material, the superposition of A.C. on D.C., agitation of the bath by steam, and of some eighteen catalysts, has been investigated. Ceric sulphate, potassium iodate, cobaltous sulphate, lead acetate, hydrofluoric acid improved considerably the current efficiency for the anodic oxidation. The probable role of these catalysts is discussed. A mechanism of the anodic oxidation of manganous sulphate in sulphuric acid is indicated.

Oxidation of manganous salts to permanganic acid, both chemically and electrolytically, seems to have been the subject of much extensive investigation (cf. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmanns Green and Co., London, 1932, Vol. XII, Part I, pp. 293, 431). The technical method for the regeneration of chromic acid in the electrolysis of chromium sulphate and sulphuric acid (cf. Askeråsy and Revai, *Z. Elektrochem.*, 1913, 19, 344) suggests the possibility of a similar method for permanganic acid. Electrolysis of manganous sulphate in the presence of sulphuric acid yields different oxidation products of manganese depending mainly upon the concentration of manganous sulphate, the temperature, and the concentration of the acid employed. Much uncertainty, however, exists, in the literature regarding the precise nature of the oxidation products obtained electrolytically (cf. Meyer, *ibid.*, 1916, 22, 201). A detailed study has, therefore, been made of the electrolysis of manganous sulphate and sulphuric acid under varied conditions (*vide infra*) with a view to defining a set of conditions for the optimal yields of oxidation products.

EXPERIMENTAL.

In all the experiments reported, manganous sulphate used was prepared from the cheap Indian material pyrolusite by its reduction with carbon and subsequent treatment with sulphuric acid under the optimum conditions, worked out by H. K. Joshi in these laboratories. The electrolysis was carried out in a cylindrical glass vessel of about 300 c.c. capacity, kept immersed in a water thermostat and maintained at the desired temperature. The electrodes used were of smooth platinum except in experiments reported in Table IX, showing the influence of anode material. The electrodes were disposed horizontally; the anode was kept at the bottom of the bath and cathode just in flush with the upper surface. Experience had shown the marked convenience of this arrangement in facilitating free escape of hydrogen and thus minimising the cathodic reduction. The circuit included a precision ammeter, electrolytic cell and suitable resistances in series and a voltmeter connected across the terminals of the electrolytic cell. The current used for the electrolysis was taken from a 220 D.C. main and was regulated by resistance bulbs and rheostats. To ascertain the optimum conditions for the oxidation, the influence of the following factors was studied over ranges as indicated below:—

Optimum conditions.

| | | | |
|---------------------------------|-----|-----|------|
| (i) Conc. of H_2SO_4 (30-90%) | ... | ... | 60% |
| (ii) Conc. of $MnSO_4$ (1.5-9%) | ... | ... | 7.5% |

| | | |
|---|-----|---------------------------|
| (iii) Temperature (15°-80°) | ... | 60° |
| (iv) Inter-electrode distance (2.9 cm) | | 5.5 cm |
| (v) Anodic C.D. (100-480 amp /dm ²) | | 300 amp/dm ² . |
| (vi) Cathodic C.D. (52-750 amp /dm ²) | | 270 amp /dm ² |
| (vii) Current conc. (0.0105-0.025) | | 0.019 amp /c.c. |

Under the optimum conditions, a study was also made of the influence of the duration of electrolysis, nature of the anode material, superposition of A.C. on D.C., of passing steam through the electrolyte during electrolysis and of the addition of a number of catalysts.

Method of Estimation of the Oxidation Products and Calculation of Current Efficiency.—A definite volume (5 c.c.) of the electrolysed solution (160 c.c.) was taken and to it was added a known excess (10 c.c.) of standard solution of (N/10) oxalic acid. The solution was then heated to about 70° and the excess of oxalic acid was back-titrated against standardised solution of N/100-KMnO₄. From this, the active oxygen content in 5 c.c. and therefore, in the total volume (160 c.c.) was computed.

The current efficiency in any experiment was calculated on the basis that 1 faraday (i.e., 26.86 amp-hours of electricity) yields 8 g. of active oxygen.

TABLE I.

Influence of sulphuric acid conc.

Electrolyte = 160 c.c. MnSO₄ = 7.5 g. in 100 c.c. soln. Current = 3 amp. Anodic C.D. = 300 amp./dm². Cathodic C.D. = 270 amp./dm². Duration = 20 min. Temp = 60°. Inter-electrode distance = 5.5 cm. P.D. = 6 volts.

5 C.c. of the electrolysed solution taken for estimation.

| Sulphuric acid in 100 c.c. soln. | Active oxygen in 5 c.c. soln (0.01 N KMnO ₄). | Total active oxygen in 160 c.c. soln. | Current efficiency |
|----------------------------------|---|---------------------------------------|--------------------|
| 30 g. | 12.2 c.c. | 0.031 g. | 10.5% |
| 45 | 59 | 0.151 | 51.0 |
| 60 | 80 | 0.205 | 69.0 |
| 75 | 35 | 0.089 | 30.0 |
| 90 | | Manganous sulphate precipitates | |

TABLE II.

Influence of manganous sulphate conc.

Conc. of H₂SO₄ = 60 g. in 100 c.c. soln. Other conditions same as in Table I.

| MnSO ₄ in 100 c.c. soln. | Active oxygen in 5 c.c. soln (0.01 N KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|-------------------------------------|--|---------------------------------------|---------------------|
| 1.5 g | 13 c.c. | 0.033g. | 11.2% |
| 3.0 | 32.7 | 0.084 | 28.2 |
| 4.5 | 45.2 | 0.116 | 39.0 |
| 6.0 | 63.5 | 0.163 | 54.8 |
| 7.5 | 80 | 0.205 | 69.0 |
| 9.0 | 81 | 0.207 | 69.9 |

TABLE III.

Effect of temperature.

Conc. of H₂SO₄ = 60 g. in 100 c.c. soln. Other conditions same as in Table I.

| Temp. | Active oxygen in 5 c.c. soln (0.01 N KMnO ₄). | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|-------|---|---------------------------------------|---------------------|
| 15° | 58 c.c. | 0.148 g. | 50.0% |
| 30 | 64 | 0.163 | 55.2 |
| 50 | 69.6 | 0.178 | 60.0 |
| 60 | 80 | 0.205 | 69.0 |
| 70 | 64.9 | 0.166 | 56.0 |
| 80 | 60.3 | 0.154 | 52.0 |

TABLE IV.

Variation of inter-electrode distance.

Conc. of H₂SO₄ = 60 g in 100 c.c. soln. Other conditions same as in Table I.

| Inter-electrode distance. | Active oxygen in 5 c.c. soln. (0.01 N KMnO ₄). | Total active oxygen in 160 c.c. soln. | Current efficiency |
|---------------------------|--|---------------------------------------|--------------------|
| 2 cm. | 69.6 c.c. | 0.178 g. | 60.0% |
| 4 | 76.5 | 0.197 | 66.0 |
| 5.5 | 80 | 0.205 | 69.0 |
| 8 | 80 | 0.205 | 69.0 |
| 9 | 80 | 0.205 | 69.0 |

TABLE V.

*Effect of current density.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Current. | Time. | Anodic C.D. amp./dm. ² | Cathodic C.D. amp./dm. ² | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|----------|---------|--------------------------------------|--|--|---|------------------------|
| 1 amps | 60 min. | 100 | 91 | 77 | 0.197 g. | 66.4% |
| 2 | 30 | 200 | 180 | 77.9 | 0.199 | 67.2 |
| 3 | 20 | 300 | 270 | 79.9 | 0.205 | 68.9 |
| 4 | 15 | 400 | 360 | 73 | 0.187 | 63.0 |
| 4.5 | 13½ | 450 | 415 | 60.3 | 0.154 | 52.0 |
| 4.8 | 12½ | 480 | 432 | 59.1 | 0.151 | 51.0 |

TABLE VI.

*Variation of cathodic current density.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Dimensions of the electrode. | Cathodic C.D. amp./dm. ² | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|------------------------------------|--|--|---|------------------------|
| 2.4 × 2.4 cm ² | 52 | 56 c.c. | 0.143 g. | 48.3% |
| 1.5 × 1.3 | 154 | 75 | 0.193 | 64.7 |
| 1.1 × 1 | 270 | 80 | 0.205 | 69.5 |
| 0.8 × 0.5 | 750 | 77.9 | 0.199 | 67.0 |

TABLE VII.

*Effect of current concentration.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Vol. of electrolyte | Current conc. amp./c.c. | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in the soln. | Current efficiency. |
|------------------------|----------------------------|--|--|------------------------|
| 120 c.c. | 0.025 | 67.1 c.c. | 0.171 g. | 57.9% |
| 160 | 0.019 | 80 | 0.205 | 69.0 |
| 200 | 0.0105 | 71.3 | 0.183 | 61.5 |

TABLE VIII.

*Effect of the duration of electrolysis.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Time. | Active oxygen in 5 c.c. soln. (0.01N- KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|--------|--|---|------------------------|
| 5 min. | 32 c.c. | 0.074 g. | 100% |
| 10 | 49 | 0.125 | 84.5 |
| 20 | 80 | 0.205 | 69.0 |
| 60 | 208.1 | 0.535 | 69.0 |
| 90 | Manganese dioxide precipitates. | | |

TABLE IX.

*Variation of anode material.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Anode material. | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency |
|---------------------|--|---|-----------------------|
| Smooth platinum | 79.9 c.c. | 0.205 g. | 68.9% |
| Platinised platinum | 58.6 | 0.149 | 50.5 |
| Lead | 87 | 0.223 | 75.0 |

TABLE X.

*Influence of superposition of A.C. on D.C.*Conc. of H_2SO_4 = 60 g. in 100 c.c. soln.

Other conditions same as in Table I.

| Conditions of the experiments | Active oxygen in 5 c.c. soln. (0.01N KMnO ₄) | Total active oxygen in 160 c.c. soln. | Current efficiency. |
|--|--|---|------------------------|
| Without superposi- tion of A.C. on D.C. | 80 c.c. | 0.205 g. | 69.0% |
| With A.C. superpos- ed on D.C. | 90.4 | 0.232 | 78.0 |

Graphite No oxidation of $MnSO_4$, Disintegration
of the electrode.

TABLE XI.

*Effect of passing steam during the electrolysis.*Conc. of $\text{H}_2\text{SO}_4 = 65.55$ g. in 100 c.c. soln. Other conditions same as in Table I.

| Conditions of the experiment. | Final volume of the soln | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄). | Total active oxygen in the soln | Current efficiency. |
|-------------------------------|--------------------------|---|---------------------------------|---------------------|
| Without passing steam | 160 c.c. | 80 c.c. | 0.05 g. | 69.0% |
| With passing steam | 178 | 52 | 0.149 | 50.0 |

TABLE XII.

*Effect of addition agents.*Conc. of $\text{H}_2\text{SO}_4 = 60$ g. in 100 c.c. soln. Amount of the addition agent = 1 g. (or c.c.) in 100 c.c. soln. Other conditions same as in Table I.

| Addition agent | P.D. in volts. | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in 160 c.c. soln | Current efficiency | Addition agent | P.D. in volts | Active oxygen in 5 c.c. soln. (0.01N-KMnO ₄) | Total active oxygen in 160 c.c. soln | Current efficiency. |
|---|----------------|--|--------------------------------------|--------------------|--|---------------|--|--------------------------------------|---------------------|
| K_2CrO_4 | 7 | 92.7 c.c. | 0.237 g. | 80.0% | $\text{Ti}(\text{SO}_4)_3$ | 7 | 80.6 c.c. | 0.206 g. | 69.5% |
| KClO_3 | 7.8 | 93.2 | 0.238 | 80.5 | $\text{H}_2\text{O}_2(\text{NO}_3)_2$ | 7.8 | 83 | 0.212 | 71.7 |
| Ag_2SO_4 | 6.7 | 83 | 0.212 | 71.6 | NaWO_4 | 7.8 | 82.3 | 0.211 | 71.0 |
| $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ | 7 | 95.5 | 0.244 | 82.4 | HF | 7.8 | 84.6 | 0.217 | 73.0 |
| H_3PO_4 | 6.7 | 79.2 | 0.203 | 69.3 | Na_2HPO_4 | 7 | 82.3 | 0.211 | 71.0 |
| $\text{K}_2\text{S}_2\text{O}_8$ | 7 | 76.9 | 0.197 | 66.4 | KF | 7.8 | 83.5 | 0.214 | 72.0 |
| KI | 7 | 73.1 | 0.189 | 63.9 | HCl | 7.5 | 60.5 | 0.155 | 52.2 |
| $\text{Ti}_2(\text{SO}_4)_3$ | 7 | 71.9 | 0.177 | 62.0 | KIO_3 | 7.8 | 77 | 0.248 | 83.6 |
| $\text{Ce}(\text{SO}_4)_3$ | 6.5 | 98 | 0.251 | 84.5 | $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ | 7.8 | 85 | 0.218 | 73.3 |

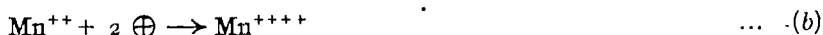
Results showing the influence on current efficiency of varying proportions of sulphuric acid and of manganous sulphate in the mixture, and of temperature are shown graphically in Fig. 1. Fig. 2 shows similarly the influence of the duration of electrolysis and of anodic and cathodic current density on the current efficiency.

DISCUSSION.

The foregoing results indicate that the anodic oxidation of manganous sulphate in presence of sulphuric acid is dependent upon a large number of parameters such as the electrolyte concentration, the current density at the anode and cathode, the temperature, the electrode material, etc. This is conveniently expressed in respect of the current efficiency which is 100% under ideal conditions. Any discrepancy in this might be ascribed to the possible disturbing factors: (i) chemical or electrochemical decomposition of the resulting product or products, (ii) occurrence of side reactions such as oxygen evolution at the anode, i.e., other than the main one for which current efficiency is calculated, or (iii) solvational effects leading partly to the formation of molecular or ionic complexes in the conducting mixtures.

When 60% sulphuric acid containing 7.5% manganous sulphate are electrolysed between the two platinum electrodes, pink colour develops at the anode instantaneously, i.e., the moment

the current is switched on (*cf.* our results). The colour deepens to dark or brown-red and deep violet on prolongation of the electrolysis due to the formation of manganic sulphate, manganese disulphate and probably traces of permanganic acid. Much uncertainty exists in the literature regarding the precise nature of the oxidation products obtained electrolytically. The considerations of the earlier workers show that the products of the anodic oxidation of manganous sulphate and sulphuric acid vary under differing conditions. A very low concentration of manganous sulphate and low temperatures are favourable for the formation of permanganic acid (*cf.* Sem, *Z. Elektrochem.*, 1915, **21**, 426; Ruscon, *Arch. Farm. Sper. Sci. aff.*, 1919, **27**, 94; Campbell, *Trans. Faraday Soc.*, 1926, **22**, 66); with higher concentrations of manganous sulphate and sulphuric acid manganic sulphate and manganic disulphate are probably formed (*cf.* Elbs, *Z. Electrochem.*, 1900, **7**, 260; Goerbig, "Beitrage zur Kenntnis der Sulphate und Nitrate des 3-bzw. 4-wertigen Mangans," Halle a.S., 1911). Meyer (*loc. cit.*) criticises several of the statements of Sem. He points out that manganic salts exist in solutions of various colours including violet, brown-red, dark green and olive-green and not only in the first two as stated by Sem. He further adds that the whole of the variously coloured solutions have practically identical absorption spectra. Consequently, he says, that Sem is not justified in subdividing manganic salts into two classes from the difference of colour. The oxidation of manganous sulphate, under the operative conditions, to manganic sulphate and manganic disulphate might possibly be represented as



in concentrated solutions.

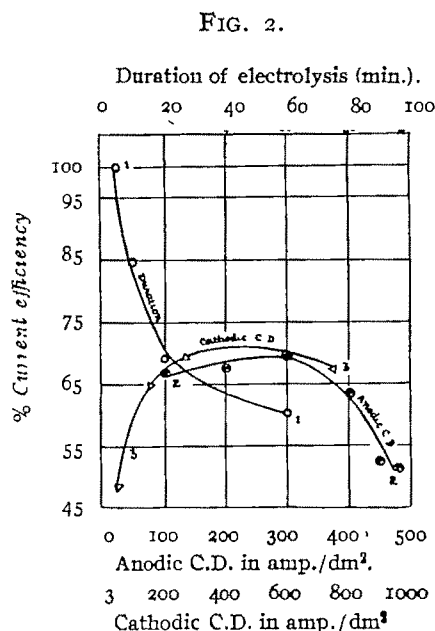
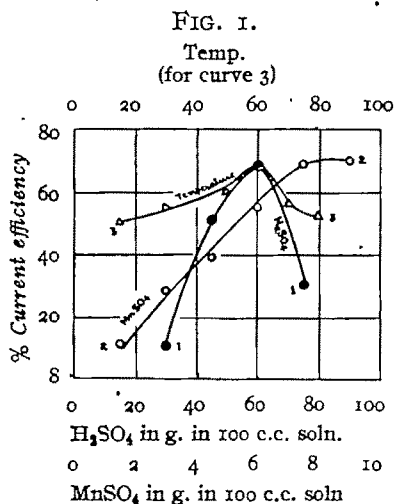
The presence of sulphuric acid plays a very important role in the anodic oxidation of manganous sulphate as is seen from the results (*cf.* Table I) of the wide variation of sulphuric acid concentration. The electrolysis of 30% sulphuric acid leads to the precipitation of manganese dioxide after a short duration, probably due to the hydrolytic decomposition of the resulting products especially in dilute acid. Very low current efficiency (10.5%) under the stated condition might probably be ascribed to the discharge of OH ion at the anode and their subsequent recombination to form water and oxygen. The current efficiency progressively increases with the concentration of sulphuric acid up to a particular limit (60%) and then diminishes (*cf.* curve 1, Fig. 1). This might probably be attributed to increased stability of the products, especially in the stronger solutions of the acid employed. A marked diminution in the current efficiency at high concentration of the acid (above 60%) appears to be chiefly due to the precipitation of manganous sulphate and its subsequent reducing action on the oxidation products formed.

As discussed previously, the concentration of manganous sulphate, the depolarizer, exerts a marked influence on the nature of the oxidation products obtained electrolytically. At very low concentration permanganic acid is formed, but in stronger solutions, manganic sulphate, manganic disulphate and other oxidation products of manganese are the chief products. In the present investigation the concentration of manganous sulphate is varied in the range 1.5–9%, the products obtained being mainly manganic sulphate and manganic disulphate and probably traces of permanganic acid. An examination of the results in Table II reveals that the yield and consequently the current efficiency of the oxidation products increase steadily (*cf.* curve 2, Fig. 1) with the concentration of manganous sulphate, the depolariser, up to a particular limit (7.5%), after which it remains almost constant with further increase in concentration. This is in agreement with the general findings in oxidation reactions. Higher concentrations (above 9%) of manganous sulphate could not be employed owing to the complications arising out of its

precipitation in strongly acid media. It should also be noted that once the precipitation of manganous sulphate occurs, the yield of oxidation products falls considerably.

Results recorded in Table III show that temperature variation (15° - 80°) has a marked influence on the current efficiency. The influence of an increase of temperature on an electrolytic oxidation, when oxygen is simultaneously being evolved, can vary. It acts favourably by increasing the velocity of diffusion of the depolariser. But it also lowers the oxygen over-voltage and thus facilitates the discharge of oxygen. According as one or the other of these two effects predominates it will be better to work at a low or a high temperature (*cf.* Allmand and Ellingham, "Principles of Applied Electro-chemistry," London, 1931, p. 104). Furthermore, the stability of the products formed needs also be considered. Thus, the rise in current efficiency (*cf.* curve 3 in Fig. 1) with the rise in temperature up to 60° (*cf.* our results) might be ascribed to increased diffusion of the depolariser and its subsequent oxidation at the anode. The diminution in yields, especially at higher temperature (above 60°), might be due to much of the current being utilised in discharging oxygen at the anode, being facilitated by lowering of its over-voltage. The reducing action of manganous sulphate on the oxidation products and the unstable nature of the latter, especially at higher temperatures, might also account for the lowering of the yields.

In any electrolytic reaction the oxidation product formed at the anode may diffuse towards the cathode and be subsequently reduced. It is to be anticipated that with the increase of inter-electrode distance up to a particular limit, the current efficiency may increase due to a diminution in reduction. Results reported in Table IV are in agreement with this deduction.



The variation of current density materially affects the anodic process. Results shown in Table V indicate that the current efficiency increases very gradually with the increase of anodic C.D. (*cf.* curve 2, Fig. 2) up to a particular limit (300 amp./dm^2), probably due to an increase in oxygen over-voltage and a corresponding diminution in its evolution. Increased rate of diffusion of the depolariser and its subsequent oxidation at the anode might also partly explain increased yields at high C.D. With further increase of C.D. (above 300 amp./dm^2) the current efficiency, however, diminishes, due presumably to increased oxygen evolution at the anode,

Results recorded in Table VI show that the current efficiency is low at low cathodic C.D. (52 amp./dm².) probably due to the fact that the oxidation products formed at the anode might be reduced appreciably by the nascent hydrogen evolved at the cathode.

The variation of current concentration affects the current efficiency of oxidation appreciably. This is illustrated from our data shown in Table VII.

As in all oxidation reactions the duration of electrolysis exerts a profound influence on the course of the anodic reaction. The oxidation of manganous sulphate in the presence of sulphuric acid is rapid and immediate as is noticed by the instantaneous formation of pink colour at the anode. The current efficiency is 100% for shorter durations (5 mins.) of electrolysis (*cf.* results in Table VIII). It shows a rapid but gradual diminution with the progress of electrolysis (*cf.* curve 1 in Fig. 2). After 1½ hours of electrolysis an immediate precipitation of manganese dioxide takes place due to increased concentration of the oxidation products and their hydrolytic decomposition.

The nature of the anode material is very important in oxidation reactions as is seen from the results recorded in Table IX. With graphite anode there was no oxidation of manganous sulphate. It appears that the whole of the current is utilised in discharging oxygen at the anode. The carbon particles produced by the disintegration of the graphite anode foul the solution. Results with smooth and platinised Pt show that better yields are obtained with the former probably due to high oxygen over-voltage. High current efficiency (75%) with Pb anode appears to be due to the catalytic influence of PbO₂ formed at the anode. Catalytic influence of the anode material, especially PbO₂, seems to have been noticed earlier. For example Regelsberger (*Z. Elektrochem.*, 1899, 6, 388) found that chromium salts, which are not oxidised at Pt anodes, are readily oxidised on the addition of a small amount of lead salts which form a PbO₂ layer on the anode (*cf.* also Muller and Soller, *Z. Elektrochem.*, 1905, 11, 863).

The chemical effects of pure alternating currents are in any case inconsiderable and not particularly remarkable. When, however, an alternating current is superposed on a direct current, some striking results are obtained (*cf.* Table X). The current efficiency improves markedly. This might probably be due to a considerable diminution in oxygen over-voltage and a corresponding lowering in the oxidising potential. The magnitude of the decrease produced in the degree of irreversibility of the direct current electrode process, depends on

(a) the ratio $\frac{\text{alternating current strength}}{\text{direct current strength}}$; (b) the frequency of the alternating current (*cf.* Allmand and Ellingham, *op. cit.* p. 147). Ghosh (*J. Amer. Chem. Soc.*, 1915, 37, 733), Stepanow (*Chem. Abst.*, 1916, 10, 2431), Archibald and Wartenberg (*Z. Elektrochem.*, 1911, 17, 812) and others have also shown that the voltage required for a particular electrolysis at a given current density will be lowered by the use of a superposed alternating current.

An examination of the results shown in Table XI reveals that the current efficiency of oxidation falls considerably (50%) by passing steam through the electrolyte. This might be accounted for as follows: The passage of steam during the electrolysis might cause a considerable agitation of the electrolyte which might produce a lowering in the oxygen over-voltage thus facilitating increased oxygen evolution at the anode. The agitation might also bring about marked decomposition of the oxidised products.

Not only the material of the electrode but also additions to the electrolyte can act as catalysts in anodic oxidations. Some of these 'oxygen-carriers' are very important. Addition of quite a large number of substances has been tried and their influence studied (*cf.* results in Table XII). Ce(SO₄)₂, KIO₃, CoSO₄, 7H₂O, KClO₃, K₂CrO₄, Pb(CH₃COO)₂, 3H₂O, HF, KF, Ag₂SO₄, etc.,

were found to be the best in descending order. The rest were found to be less promising ; while agents like $Tl_2(SO_4)_3$, KI and HCl were found to be detrimental or negative catalysts. Addition of 1 c.c. of conc. HCl to 100 c.c. of the solution, for example, lowers the current efficiency from 69% to 52.2%. This appears to be due to the oxidation of the addendum by the powerful oxidising products formed. The addition of 1 g. of $Ce(SO_4)_2$ in 100 c.c. solution raises the efficiency to a considerable extent (84.5%). This might be due to the fact that the catalyst being a powerful oxidising agent oxidises the depolariser ; it gets subsequently reoxidised at the anode and is used up again in oxidising the depolariser, the result of the whole cyclic operation being the increased oxidation of manganous sulphate. High efficiency (82.4%) of oxidation with the addition of $CoSO_4 \cdot 7H_2O$ can be explained in a somewhat similar manner. Cobaltous sulphate may be oxidised to cobaltic sulphate ($Co^{++} \rightarrow Co^{+++}$) which may subsequently react with the depolariser regenerating cobaltous sulphate. Increased efficiency with the addition of $KClO_3$, K_2CrO_4 and of KIO_3 might possibly be attributed to their high oxidising property. Favourable effects of $Pb(CH_3COO)_2 \cdot 3H_2O$ might be ascribed to the catalytic influence of PbO_2 film formed at the anode, as discussed previously. Addition of 1 c.c. of HF in 100 c.c. solution raises the current efficiency from 69% to 73%, probably due to a considerable rise in the anode potential. The results with the addition of KF can be explained on similar lines. The mode of action of the catalysts is clear and simple in some cases but sometimes this is not so. The work of earlier investigators leads to similar conclusions.

In conclusion the authors express their indebtedness to Prof. S. S. Joshi for suggesting the problem and giving valuable help and criticism during the course of this investigation.

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THE CONDENSATION OF α -SUBSTITUTED ACETOACETATES WITH PHENOLS. PART VI. THE CONDENSATION OF PHENOLS WITH ETHYL ACETOSUCCINATE

BY R. H. SHAH AND N. M. SHAH.

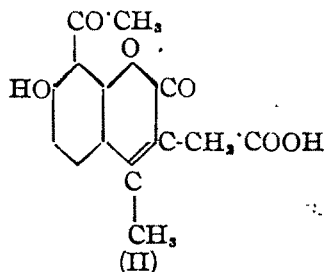
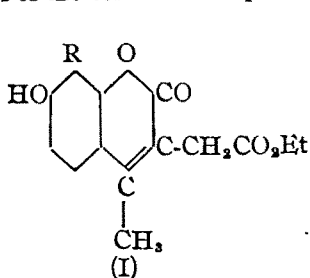
The Pechmann condensation of several phenols with ethyl acetosuccinate in presence of different condensing agents has been studied with a view to finding the effect of $-\text{CH}_2\text{COOEt}$ as α -substituent on the course of the reaction. Reactive phenols like resorcinol, orcinol, etc., easily undergo the condensation. Various coumarin-3-acetic acids and their derivatives have been synthesised. Of the less reactive phenols, *m*-cresol and β -naphthol condense with the formation of the corresponding coumarin derivatives.

In extension of the previous work on the condensation of α -substituted acetoacetates (with α -substituents other than alkyl) with phenols (Shah and Shah, *Ber.*, 1938, 71, 2075; Shah, *J. Univ. Bombay*, 1939, 8, 205; Kulkarni, Alimchandani and Shah, *J. Indian Chem. Soc.*, 1941, 18, 113, 123; Shah and Kulkarni, *J. Univ. Bombay*, 1941, 10, 86), the present investigation was undertaken with a view to study systematically the effect of carboethoxy-methyl (CH_2COOEt) group as an α -substituent in the acetoacetate molecule on its reactivity in the Pechmann condensation. This communication describes the results of the condensation of ethyl acetosuccinate with several phenols under the conditions of Pechmann and Simonis reactions as well as in the presence of other condensing agents.

Condensation of ethyl acetosuccinate with reactive phenols like resorcinol, pyrogallol, orcinol, α -naphthol and phloroglucinol.—The condensation of resorcinol with ethyl acetosuccinate in presence of sulphuric acid has been described by several investigators (Bannerjee, *J. Indian Chem. Soc.*, 1931, 8, 777; Dey and Sankaranarayanan, *ibid.*, p. 819; Chakravarti, *ibid.*, 1935, 12, 538). We have now further investigated this condensation in the presence of (1) aluminium chloride, (2) phosphorus oxychloride and (3) phosphoric anhydride. In all cases, the coumarin derivative identical with one obtained by using sulphuric acid is obtained. 7-Hydroxy-4-methylcoumarin-3-acetic acid is obtained directly in good yield, with aluminium chloride as condensing agent, the expected ester being hydrolysed during the reaction. Phosphoric anhydride gives the same coumarin as its ester (I; $\text{R}=\text{H}$) in very poor yield; while phosphorus oxychloride produces the same ester (I, $\text{R}=\text{H}$) in excellent yield. It is noteworthy that in this as well as in subsequent condensations described here, the oxychloride has been found to be a very efficient condensing agent, giving the maximum yields of the condensation products.

Ethyl 7-hydroxy-4-methylcoumarin-3-acetate (I, $\text{R}=\text{H}$) on hydrolysis gives the acid identical with the acid obtained by aluminium chloride method. This acid is stable and cannot be decarboxylated by heating above its melting point. However, the de-carboxylation is effected by quinoline-copper method, using its acetyl derivative. The product obtained is identical with 7-hydroxy-3 : 4-dimethylcoumarin, the de-acetylation having occurred during the reaction.

Ethyl 7-acetoxy-4-methylcoumarin-3-acetate on Fries migration with aluminium chloride gives 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetic acid (II) identical with the acid obtained by the hydrolysis of the condensation product of 2-acetyl-resorcinol with ethyl acetosuccinate.



Orcinol on condensation with ethyl acetosuccinate in the presence of phosphorus oxychloride gives an excellent yield of ethyl 5-hydroxy-4 : 7-dimethyl-coumarin-3-acetate (III ; $R = CH_3$), from which the corresponding coumarin-3-acetic acid is obtained by hydrolysis.

Pyrogallol on similar condensation gives ethyl 7 : 8-dihydroxy-4-methylcoumarin-3-acetate (I, $R = OH$). Sulphuric acid as condensing agent has been found to hydrolyse the ester giving directly the acid (*cf.*, Chakravarti, *loc. cit.*). Aluminium chloride does not give any condensation product. Attempts to decarboxylate the acid as well as the Fries transformation of 7 : 8-diacetoxycoumarin derivative have been unsuccessful.

The condensation of α -naphthol has been studied in presence of sulphuric acid, phosphorus oxychloride and pentoxide as well as aluminium chloride. In all cases, 4-methyl- α -naphthapyrone-3-acetic acid or its ethyl ester identical with those of the previous workers (Bannerjee, *loc. cit.* Dey and Sadkaranarayanan, *loc. cit.*) is obtained.

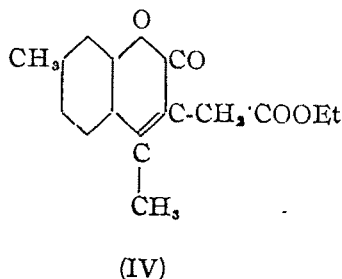
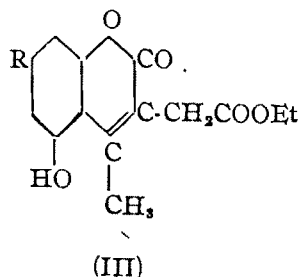
Phloroglucinol condenses smoothly in presence of sulphuric acid (80%) as well as phosphorus oxychloride. The acid is found to hydrolyse the ester giving the corresponding acid ; the oxychloride gives an excellent yield of ethyl 5 : 7-dihydroxy-4-methylcoumarin-3-acetate (III, $R = OH$) which on hydrolysis gives the corresponding coumarin-3-acetic acid.

The coumarin-3-acetic acids described here are very stable and are not easily decarboxylated in contrast to coumarin-4-acetic acids which easily lose carbon dioxide on heating (Dey and Row, *J. Indian Chem. Soc.*, 1924, 1, 107, 22 *et seq.*). These acids do not react with aromatic aldehydes according to Knoevenagel reaction. An explanation in terms of induced alternate polarities for the reduced reactivity of coumarin-3-acetic acids (Bannerjee, *loc. cit.*) satisfactorily explains the behaviour of these acids studied in this investigation.

m-Cresol condenses with ethyl acetosuccinate with sulphuric acid as condensing agent. It is interesting to note that the change of temperature affects the condensation considerably. Ethyl 4 : 7-dimethylcoumarin-3-acetate (IV) may be obtained by keeping the reaction mixture well cooled. If the temperature is not properly kept down or the condensation carried out in summer months, a product, m.p. 135° , identical with 4 : 7-dimethylcoumarin, is obtained. It is noteworthy that the substituent is totally eliminated under the experimental conditions. A similar elimination of $-CH_2.COOEt$ has also been observed in case of methyl β -resorcyate condensation (see next paper). Neither phosphorus oxychloride nor pentoxide could affect the condensation, unchanged cresol being obtained.

β -Naphthol gives on condensation in presence of sulphuric acid (but not in presence of phosphorus oxychloride or phosphorous pentoxide) 4-methyl- β -naphthapyrone-3-acetic acid identical with that of Dey and Sankaranarayanan (*J. Indian Chem. Soc.*, 1931, 8, 825). β -Naphthapyrone-3-acetic acid cannot be decarboxylated.

o-Cresol, *p*-cresol, quinol, phenol and catechol do not undergo condensation with ethyl acetosuccinate.



E X P E R I M E N T A L.

Condensation of Resorcinol with Ethyl Acetosuccinate: Formation of 7-Hydroxy-4-methyl-coumarin-3-acetic acid and its Ethyl Ester.

(i) Resorcinol (5 g.) was mixed with ethyl acetosuccinate (10 g.) and phosphorus oxychloride (3 c.c.) gradually added with stirring and cooling. After sometime the mixture solidified; it was left at room temperature overnight. It was treated with cold water and the solid crystallised from alcohol as needles, m.p. 163° , yield nearly theoretical. Bannerjee (*loc. cit.*) and Dey and Sankaranarayanan (*loc. cit.*) give m.p. 162° and 163° respectively; mixed m.p. with the ester obtained by using sulphuric acid as a condensing agent according to the above authors was undepressed.

(ii) The condensation was carried out in presence of P_2O_5 (20 g.) (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1935, **12**, 538). The product obtained in low yield was identical with the above ester, m.p. and mixed m.p. 163° .

The acetyl derivative crystallised from alcohol as shining plates, m.p. 98° .

The benzoyl derivative crystallised from alcohol and then from chloroform-benzene mixture as shining needles, m.p. 138° . Bannerjee (*loc. cit.*) gives m.p. 127° .

(iii) To a solution of aluminium chloride (5.5 g., 2 mols.) in dry nitrobenzene (30 c.c.), resorcinol (3 g., 1 mol.) and the ester (6 g., 1 mol.) were added and the mixture, protected from moisture by $CaCl_2$ guard tube, was heated on an oil-bath for 1 hour. Copious hydrochloric acid fumes were evolved. After the reaction subsided, the mixture was cooled and distilled in steam after adding ice and concentrated hydrochloric acid (10 c.c.). The residual liquid was freed from some tarry matter and on cooling it deposited needle-shaped crystals, m.p. $265-66^{\circ}$, mixed m.p. with the acid obtained by the hydrolysis of the ester was undepressed, yield 8.5 g. Both the acid and the ester dissolve in alkaline solution with blue fluorescence. The acetyl derivative, prepared by acetic anhydride and a drop of sulphuric acid, crystallised from hot water, m.p. $199-200^{\circ}$. (Found: Equiv., 274.8. $C_{14}H_{12}O_6$ requires Equiv., 276).

The benzoyl derivative crystallised from alcohol, m.p. $190-91^{\circ}$. (Found: C, 67.4; H, 4.2. $C_{18}H_{14}O_6$ requires C, 67.45; H, 4.14 per cent).

Decarboxylation of the Acid.—7-Acetoxy-4-methylcoumarin-3-acetic acid (1 g.) was mixed with quinoline (15 c.c.), copper-bronze (0.3 g.) and refluxed for nearly 45 minutes with a low flame. Copper was removed, the filtrate mixed with excess of dilute hydrochloric acid and extracted with ether; the ethereal extract washed with sodium bicarbonate solution, the ethereal layer separated, dried and ether removed. The brown solid was dissolved in dilute sodium hydroxide, filtered and the filtrate acidified; the solid crystallised from alcohol, m.p. 254° , mixed m.p. with authentic sample unchanged. The acetyl derivative melts at 164° . Pechmann and Duisberg (*Ber.*, 1883, **16**, 2119) give m.p. 165° .

Fries Transformation.—Ethyl 7-acetoxy-4-methylcoumarin-3-acetate (2 g.) was intimately mixed with aluminium chloride (7.8 g.) and heated on an oil-bath at $120-25^{\circ}$ for 2 hours. It was then cooled and treated with ice-cold water acidified with hydrochloric acid. The solid was collected and crystallised from alcohol, m.p. $256-57^{\circ}$. The product was identical with 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetic acid (*vide* next paper).

The acid dissolves in alkali with yellowish colour without any fluorescence and gives red colour with alcoholic ferric chloride.

Condensation of Orcinol: Formation of Ethyl 5-hydroxy-4:7-dimethylcoumarin-3-acetate.—Anhydrous orcinol (2 g.) was condensed with ethyl acetosuccinate (3.5 g.) in presence of phosphorus oxychloride (2 c.c.). It was then worked up as before. The product crystallised from

alcohol as needles, m.p. 206° , yield 3 g. (Found: C, 64.8; H, 5.5. Calc. for $C_{15}H_{10}O_6$: C, 65.2; H, 5.8 per cent). Chakravarti (*loc. cit.*) gives m.p. $198-200^{\circ}$. The same condensation was repeated in presence of sulphuric acid and the product was obtained in less yield. It dissolves in alkali solution with non-fluorescent yellow colour.

The *acetyl* derivative crystallised from alcohol as needles, m.p. $91-92^{\circ}$. (Found: C, 64.0; H, 5.9. $C_{17}H_{12}O_6$ requires C, 64.15; H, 5.7 per cent).

5-Hydroxy-4: 7-dimethylcoumarin-3-acetic Acid.—The above ester (1 g.) was boiled with 2N-NaOH (20 c.c.) on a water-bath for 15 minutes; it was cooled, acidified and the solid collected and crystallised from alcohol as lustrous plates, m.p. 270° . (Found: Equiv., 120. $C_{18}H_{12}O_6$ requires Equiv., 248). Evidently the pyrone ring has opened and the acid titrates as dibasic acid.

The *acetyl* derivative crystallised from dilute alcohol, m.p. $183-84^{\circ}$. (Found: C, 62.0; H, 4.9. $C_{15}H_{14}O_6$ requires C, 62.1; H, 4.8 per cent).

Condensation of Pyrogallol: Formation of 7: 8-Dihydroxy-4-methylcoumarin-3-acetic Acid and its Ethyl Ester.

(i) Pyrogallol (4 g.) was mixed with ethyl aceto-succinate (7 g.) and concentrated sulphuric acid (20 c.c.) slowly added with cooling under tap; the mixture left overnight and then poured into cold water with stirring. No solid separated. On scratching the sides of the beaker, the solid began to come down slowly; it was collected after some time and crystallised from dilute acetone as needles, m.p. 240° . (dried sample, m.p. 270°). (Found: C, 57.8; H, 4.1. $C_{12}H_{10}O_6$ requires C, 57.6; H, 4.1 per cent). The acid dissolves in alkali and concentrated sulphuric acid with lemon-yellow colour. The acid was also obtained by the hydrolysis of the ester obtained below.

The *acetyl* derivative crystallised from dilute acetic acid, m.p. $224-25^{\circ}$. (Found: C, 57.3; H, 4.1. $C_{16}H_{14}O_6$ requires C, 57.5; H, 4.2 per cent).

(ii) To prevent hydrolysis, the above condensation was repeated at lower temperature by keeping it in ice. The product obtained crystallised from dilute acetone as needles, m.p. 206° , yield 1 g. (Found: C, 60.4; H, 5.4. $C_{14}H_{14}O_6$ requires C, 60.44; H, 5.04 per cent). Chakravarti (*loc. cit.*) gives m.p. 186° .

The ester dissolves in alkali with deep orange colour and gives with alcoholic ferric chloride green colour.

(iii) An excellent yield of the above ester was obtained by carrying out the above condensation with phosphorus oxychloride as condensing agent.

The *acetyl* derivative crystallised from alcohol as fine needles, m.p. $123-24^{\circ}$. (Found: C, 60.2; H, 5.2. $C_{18}H_{18}O_6$ requires C, 59.7; H, 5.0 per cent).

Condensation of Phloroglucinol: Formation of 5: 7-Dihydroxy-4-methylcoumarin-3-acetic Acid and its Ethyl Ester.—Anhydrous phloroglucinol (2 g.), ethyl aceto-succinate (3.5 g.) and phosphorus oxychloride (2 c.c.) were mixed with cooling under tap, and left overnight. The mixture was found solidified. It was worked up as before. The solid crystallised from alcohol as needles, m.p. 250° , yield about 4 g. (Found: C, 60.1; H, 4.95. $C_{14}H_{14}O_6$ requires C, 60.4; H, 5.03 per cent). It dissolves in alkali and concentrated sulphuric acid with greenish colour.

The *acetyl* derivative crystallised from alcohol as lustrous needles, m.p. $114-15^{\circ}$. (Found: C, 59.5; H, 4.83. $C_{18}H_{18}O_6$ requires C, 59.7; H, 5.0 per cent).

Hydrolysis of the Ester.—The ester (1 g.) was heated with 2N-NaOH (20 c.c.) for 20 minutes on a water-bath. It was then acidified; the solid crystallised from boiling water to which few drops of alcohol were added, m.p. above 285° . (Found: C, 57.5; H, 4.1. $C_{12}H_{10}O_6$ requires C, 57.6; H, 4.0 per cent). The same acid was directly obtained by condensing phloroglucinol with sulphuric acid (80%) as condensing agent.

The *acetyl* derivative crystallised from alcohol as needles, m.p. 169.70° . (Found: C, 57.4; H, 4.3. $C_{16}H_{14}O_4$ requires C, 57.5; H, 4.2 per cent).

Condensation of α -Naphthol: Formation of 4-Methyl- α -naphthapyrone-3-acetic Acid and its Ethyl Ester.

α -Naphthol was condensed in presence of different condensing agents as before; the results are summarised below.

| Condensing agent. | Product obtained. | Remarks. |
|-------------------|---|---|
| Conc. H_2SO_4 | Ethyl 4-methyl- α -naphthapyrone-3-acetate, m.p. 141° | Bannerjee (<i>loc. cit.</i>) gives m.p. 137° . Very low yield. |
| P_2O_5 | " " | " |
| H_2SO_4 (80%) | 4-Methyl- α -naphthapyrone-3-acetic acid, m.p. $253-254^{\circ}$. | (Found: Equiv., 262. $C_{16}H_{12}O_4$ requires Equiv. 268). |
| $AlCl_3$ | " " | " |
| $POCl_3$ | " " | A coloured pasty mass was obtained which was worked up, yield 1.5 g. from 2 g α -naphthol. |

Condensation of m-Cresol: Formation of Ethyl 4:7-Dimethylcoumarin-3 acetate.—*m-Cresol* (5 g.) and ethyl aceto-succinate (10 g.) were mixed and concentrated sulphuric acid (20 c.c.) slowly added with cooling in ice. The mixture was left overnight in a vessel containing ice. It was then worked up by adding ice-water and the solid collected and crystallised from alcohol as needles, m.p. 106° , yield 3 g. (Found: C, 69.0; H, 5.9. $C_{18}H_{16}O_4$ requires C, 69.2; H, 6.1 per cent).

4:7-Dimethylcoumarin-3-acetic Acid.—The ester (1 g.) was hydrolysed by heating on a water-bath with 2*N*-NaOH (20 c.c.). It was cooled and acidified and the solid separating crystallised from boiling water as fine lustrous needles, m.p. $193-94^{\circ}$. (Found: Equiv., 233.3. $C_{18}H_{14}O_4$ requires Equiv., 232).

Condensation of β -Naphthol: Formation of 4-Methyl- β -naphthapyrone-3-acetic Acid.—The mixture of β -naphthol (4 g.) and ethyl aceto-succinate (7 g.) was treated with concentrated sulphuric acid (12 c.c.) with cooling and left overnight. It was worked up as before. The substance crystallised from dilute alcohol as yellowish needles, m.p. 199° , yield 3 g. (Found: Equiv., 273. $C_{18}H_{14}O_4$ requires Equiv., 268). Dey and Sankaranarayanan (*loc. cit.*) give the same melting point.

The *ethyl ester* crystallised from alcohol, m.p. 101° .

We thank Dr. M. S. Shah. Our grateful thanks are due to Dr. R. C. Shah for his sympathetic and kind interest.

THE MADHAVALAL RANCHHODLAL SCIENCE INSTITUTE,
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THE CONDENSATION OF α -SUBSTITUTED ACETOACETATES WITH PHENOLS. PART VII THE CONDENSATION OF VARIOUS SUBSTITUTED PHENOLS WITH ETHYL ACETOSUCCINATE.

BY R. H. SHAH AND N. M. SHAH.

In continuation of Part VI, ethyl acetosuccinate has been condensed with various substituted phenols, having $-\text{COOMe}$, $\text{CO}-\text{R}$ ($\text{R}=\text{Me}$, Ph), $-\text{NO}_2$, halogens as substituents. The effect of these substituents on the course of the reaction has been discussed.

In the preceding part of this series (Part VI), the authors showed that ethyl acetosuccinate condenses with different phenols giving the coumarin-3-acetic acid derivatives. With a view to study the effect of different substituents in a phenol molecule, the condensation of ethyl acetosuccinate with several substituted phenolic derivatives was undertaken and the results are described in this part. The reactivity of the following substituents $-\text{COOMe}$, COMe , $\text{CO}\cdot\text{Ph}$, $-\text{NO}_2$ and halogens on the course of the reaction has been studied.

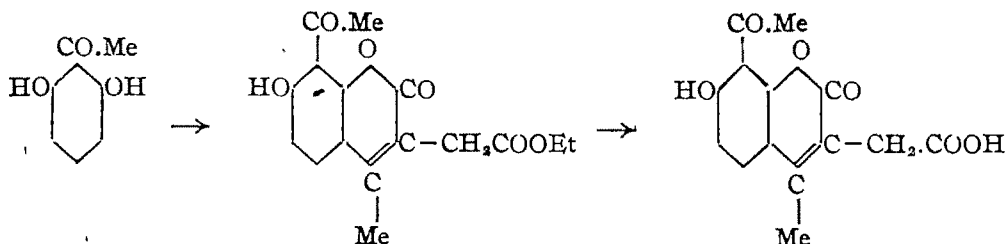
Methyl β -resorcyate on condensation with ethyl acetosuccinate in the presence of sulphuric acid gives methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (Shah, Sethna *et al*, *J. Indian Chem. Soc.*, 1937, **14**, 717). The expected ethyl 7-hydroxy-6-carbomethoxy-4-methylcoumarin-3-acetate could not be obtained in spite of several attempts. It may be pointed out that the group CH_2COOEt is eliminated in this condensation as in case of *m*-cresol described in the previous part. Phosphoryl chloride also gives the same product in lesser yield.

2-Acetyl-resorcinol easily undergoes the condensation in presence of sulphuric acid as well as phosphorus oxychloride. Sulphuric acid is found to hydrolyse the product giving the coumarin-3-acetic acid directly; while the oxychloride gives ethyl 7-hydroxy-8-acetyl-4-methyl coumarin-3-acetate which on hydrolysis gives the above acid, identical with the Fries migration product of 7-acetoxy-4-methylcoumarin-3-acetate (*vide* previous paper). This condensation of 2-acetyl-resorcinol was studied by Shah and Jatti (*Proc. Indian Sci. Cong.*, 1940, 65) in presence of aluminium chloride with the production of identical coumarin derivatives.

Similarly, 2-benzoyl-resorcinol smoothly undergoes condensation yielding ethyl 7-hydroxy-8-benzoyl-4-methyl coumarin-3-acetate.

Resacetophenone and resbenzophenone do not condense with ethyl acetosuccinate. The deactivating effect of acyl group in 2-position of the resorcinol nucleus is negligible; whereas the same in the 4-position is very great as resacetophenone and other 4-acyl-resorcinols do not condense even with unsubstituted acetoacetate in presence of sulphuric acid (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, **228**, 1424 and subsequent papers).

In order to find the effect of nitro group, the condensation of 2- and 4-nitro-resorcinols was tried but unchanged phenols were recovered.



Clayton (*J. Chem. Soc.*, 1908, 2018) generalised that the presence of halogen atom in the phenolic nucleus hinders the Pechmann reaction. It seemed, therefore, of interest to study the behaviour of halogenated phenols with ethyl acetosuccinate. 4-Chloro-phenol, 4-chloro-*m*-cresol, 4-chloro-resorcinol, 4-bromo-resorcinol and 4-chloro- α -naphthol have been tried. 4-Chloro-phenol does not condense: this is in conformity with the usual less reactivity of *para*-substituted phenols in the Pechmann reaction. All the remaining halogenated phenols condense with ethyl acetosuccinate giving the corresponding coumarin-3-acetic acid derivatives. It is interesting to note that 4-bromo-resorcinol gives ethyl 7-hydroxy-4-methyl-coumarin-3-acetate. This elimination of bromine during the condensation is noteworthy. As far as we are aware, it is a singular instance of halogen elimination in the Pechmann reaction.

From the results described here and in the previous part, it is found that the classification of phenols with regard to their reactivity with β -ketonic esters in Pechmann reaction holds good in case of ethyl acetosuccinate also. *m*-Cresol and β -naphthol give coumarins in good yields. No chromone derivative has been obtained in any case even with less reactive phenols in presence of phosphorus pentoxide. It is evident from the results that in spite of the heavier bulk of its α -substituent, the acetosuccinate is equally or even more reactive than the corresponding simple α -alkyl substituted acetoacetate. The introduction of the negative group like carboethoxy in the alkyl group has tended to increase the reactivity of the ester which may be attributed to its greater enolisation. Similar observations have also been made in case of the Pechmann condensation of phenols with ethyl α -acetoglutarate, the next homologue of ethyl acetosuccinate (Shah and Shah, *Ber.*, 1938, 74, 2075).

EXPERIMENTAL.

Condensation of Methyl β -resorcylate with Ethyl acetosuccinate.—Methyl β -resorcylate (4g.) was mixed with ethyl acetosuccinate (5 g.) and sulphuric acid (80% ; 25 c.c.) gradually added. The mixture was left overnight and worked up as usual. A pasty mass separated, and on washing with little alcohol it gave a white solid, which crystallised from alcohol, m.p. 213-214°, yield 3 g., mixed m.p. with methyl 7-hydroxy-4-methylcoumarin-6-carboxylate was unchanged.

The condensation was repeated several times under different conditions to get the expected coumarin-3-acetic acid but the product obtained was identical with the above, the elimination of CH_2COOEt taking place.

The *acetyl* derivative crystallised from alcohol as needles, m.p. 172-173°, mixed m.p. with an authentic sample.

Condensation of 2-Acetyl-resorcinol: Formation of Ethyl 7-hydroxy-8-acetyl-4-methyl-coumarin-3-acetate.—To the mixture of 2-acetylresorcinol (1 g.) and ethyl acetosuccinate (1.5 g.), phosphorus oxychloride (2 c.c.) was added with cooling and after about 20 hours, it was worked up; the yellowish solid was collected and crystallised from alcohol as needles, m. p. 167°-168°. (Found: C, 63.1. H, 5.4. $\text{C}_{16}\text{H}_{14}\text{O}_6$ requires C, 63.2; H, 5.3 per cent). The coumarin dissolves in alkali with non-fluorescent yellow colour and gives violet colour with alcoholic ferric chloride.

The *acetyl* derivative crystallised from alcohol as thin plates, m. p. 221-223°. (Found: C, 63.3; H, 5.1. $\text{C}_{16}\text{H}_{14}\text{O}_7$ requires C, 62.5; H, 5.2 per cent).

Hydrolysis of the above Ester.—The ester (0.5 g.) was treated with 2 *N*-sodium hydroxide (10 c.c.) on a water-bath for about 20 minutes. It was cooled and acidified; the solid crystallised from alcohol as needles, m. p. 262-263°. (Found: C, 60.8; H, 4.7. $\text{C}_{14}\text{H}_{12}\text{O}_6$ requires C, 60.9; H, 4.4 per cent). 7-Hydroxy-8-acetyl-4-methylcoumarin-3-acetic acid gives wine-red colour with ferric chloride.

The same acid was directly obtained by condensing 2-acetyl-resorcinol in presence of 80% sulphuric acid.

Condensation of 2-Benzoylresorcinol: Formation of Ethyl 7-Hydroxy-8-benzoyl-4-methylcoumarin-3-acetate.—2-Benzoyl-resorcinol (1 g.), ethyl aceto-succinate (2 g.) and phosphorus oxychloride (2 c.c.) were condensed as in the preceding case. The product was crystallised from alcohol as rectangular plates, m. p. 196-197°. (Found: C, 65.92; H, 4.85. $C_{21}H_{18}O_7$ requires C, 65.97; H, 4.7 per cent). The coumarin is soluble in common organic solvents and dissolves in alkali with non-fluorescent yellow colour and gives red colour with alcoholic ferric chloride.

The acetyl derivative crystallised from alcohol as rhombic crystals, m. p. 177°. (Found: C, 65.0; H, 4.8. $C_{23}H_{20}O_8$ requires C, 65.1; H, 4.7 per cent).

7-Hydroxy-8-benzoyl-4-methylcoumarin-3-acetic Acid.—The ester (1 g.) was mixed with 2 N-sodium hydroxide (25 c.c.) and kept at room temperature for 24 hours. It was then acidified and the solid dissolved in sodium bicarbonate solution, filtered and the filtrate acidified; the acid crystallised from dilute alcohol as small needles, m. p. 255°. (Found: C, 64.3; H, 4.0. $C_{19}H_{14}O_7$ requires C, 64.4; H, 3.9 per cent).

Condensation of 4-Chloro- α -naphthol: Formation of 6-chloro-4-methyl-1:2- α -naphthapyrone-3-acetic Acid and its Ethyl Ester.—To the mixture of 4-chloro- α -naphthol (4 g.) and the ester (5 g.) concentrated sulphuric acid (20 c.c.) was gradually added with shaking and cooling. The product, isolated as before, crystallised from alcohol as needles, m.p. 185-86°, yield 2 g. Chakravarti and Bagchi (*J. Indian Chem. Soc.*, 1936, 18, 655) give m.p. 181-184°. (Found: Cl, 11.05. Calc. for $C_{18}H_{15}O_4$ Cl: Cl, 10.75 per cent).

The ester was hydrolysed as before. The acid crystallised from acetic acid as needles, m.p. 276-277°. (Found: Equiv., 301.7; Cl, 11.85. $C_{18}H_{11}O_4$ Cl requires Equiv., 302; Cl, 11.73 per cent). The same acid was obtained directly if the condensation was carried out using 80% sulphuric acid.

The anilide crystallised from alcohol as thin lustrous needles, m.p. 265-66°. (Found: Cl, 9.5. $C_{22}H_{15}O_3$ NCl requires Cl, 9.4 per cent).

Condensation of 4-Chloro-resorcinol: Formation of 7-Hydroxy-6-chloro-4-methylcoumarin-3-acetic Acid and its Ethyl Ester.—To the mixture of resorcinol (2.5 g.) and ethyl aceto-succinate (4 g.), concentrated sulphuric acid (10 c.c.) was added with cooling in ice. The product obtained as before crystallised from acetic acid as small needles, m.p. 174°. Chakravarti (*J. Indian Chem. Soc.*, 1935, 12, 626) gives the same m. p. The coumarin gives intense blue fluorescence in alkaline solution.

The acetyl derivative crystallised from alcohol as needles, m.p. 169°. (Found: Cl, 10.65. $C_{18}H_{15}O_4$ Cl requires Cl, 10.49 per cent).

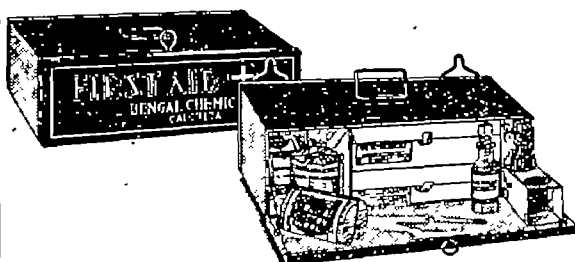
Phosphorus oxychloride also effects this condensation.

The above ester was refluxed with 2 N-sodium hydroxide (20 c.c.) for about $\frac{1}{2}$ an hour. The acid was isolated as usual and crystallised from dilute alcohol as needles, m.p. 263°. (Found: Cl, 13.14. $C_{12}H_9O_3$ Cl requires Cl, 13.2 per cent).

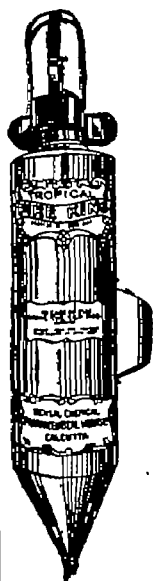
Condensation of 4-Bromoresorcinol.—4-Bromo-resorcinol was prepared according to method described in *Org. Syn.* (1937, 17, 23). To the mixture of resorcin (4 g.) and ethyl aceto-succinate (5 g.), phosphorus oxychloride was slowly added with cooling. The mixture was worked up as before. The product obtained was found to be ethyl 7-hydroxy-4-methylcoumarin-3-acetate, the de-bromination having occurred during the course of the reaction. Sulphuric acid as condensing agent gave an uncrystallisable product.

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THE CONDENSATION OF α -SUBSTITUTED ACETO ACETATES WITH PHENOLS.

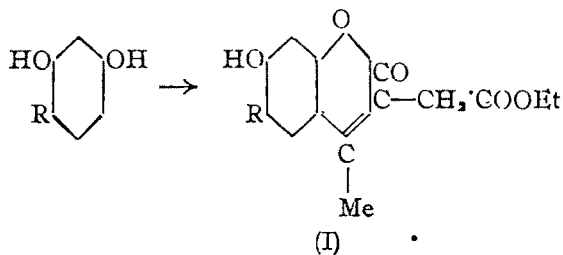
PART VIII. THE CONDENSATION OF C-ALKYL-RESORCINOLS AND ETHYLPYROGALLOL WITH ETHYL ACETOSUCCINATE.

BY R. H. SHAH AND N. M. SHAH.

The condensation of C-alkyl-resorcinols and ethyl pyragallool with ethyl acetosuccinate has been described. Various coumarin-3-acetic acids derived from the above phenols and their derivatives have been obtained

In continuation of our investigations on the reactivity of ethyl acetosuccinate in its Pechmann condensation described in the preceding parts of this series (Parts VI and VII), the present work was undertaken in order to synthesise coumarin-3-acetic acids from C-alkyl-resorcinols and to study the reactivity of the above ester in its Pechmann reaction with C-alkyl-resorcinols.

The condensation of 4-ethylresorcinol with ethyl acetosuccinate in presence of sulphuric acid proceeds smoothly and the product obtained is ethyl 7-hydroxy-6-ethyl-4-methylcoumarin-3-acetate (I, R=Et), m.p. 184-85°, the course of reaction being represented below:



The ester (I, R=Et) is hydrolysed to the corresponding coumarin-3-acetic acid. This acid is stable and attempts to decarboxylate it are unsuccessful.

Similarly, 4-methyl-, 4-propyl-, 4-butyl-resorcinols are condensed and the products obtained are ethyl 7-hydroxy-6-alkyl-4-methylcoumarin-3-acetate (I; R=Me, Pr, Bu) and the corresponding acids have been obtained by hydrolysis.

All the condensation products dissolve in alkali with blue fluorescence characteristic of 7-hydroxycoumarin derivatives. To study the effect of the change of the condensing agent, sulphuric acid has been substituted by phosphorus oxychloride. In all cases, the condensation in the presence of the oxychloride proceeds easily at ordinary temperature even without a solvent, the identical coumarins being obtained in far greater yields.

The behaviour of 4-ethylpyrogallol is similar to that of 4-ethylresorcinol; it condenses smoothly with ethyl acetosuccinate in presence of phosphorus oxychloride giving an excellent yield of ethyl 7:8-dihydroxy-6-ethyl-4-methylcoumarin-3-acetate.

It is seen from the above that the condensation is effected as easily as in case of unsubstituted resorcinol and pyrogallol. The alkyl group in 4-position of the resorcinol and pyrogallol nucleus has practically very little or no retarding influence on the course of the reaction.

E X P E R I M E N T A L.

Ethyl 7-Hydroxy-6-ethyl-4-methylcoumarin-3-acetate.—4-Ethylresorcinol required for this work was prepared by the Clemmensen reduction of resacetophenone using the modified method of Robinson and Shah (*J. Chem. Soc.*, 1934, 1494).

(i) 4-Ethylresorcinol (2.5 g.) was mixed with ethyl acetosuccinate (4 g.) and sulphuric acid (80%, 10 c.c.) slowly added with cooling. The mixture was then left overnight and worked up by adding into ice-cold water; the solid was collected, washed with water and crystallised from alcohol as fine plates, m.p. 183-84°, yield 2 g.

(ii) The above condensation was carried out in presence of phosphorus oxychloride (2 c.c.). Next day the mixture was treated with water; the solid crystallised from alcohol as fine plates, yield 48., m.p. and mixed m.p. with the above sample, 185°. (Found: C, 65.7; H, 6.6. $C_{16}H_{12}O_6$ requires C, 66.2; H, 6.2 per cent). The coumarin is soluble in acetic acid, hot alcohol, benzene and chloroform; insoluble in petroleum ether. It gives bright blue fluorescence in alkali solution and in concentrated sulphuric acid.

The *acetyl* derivative, prepared by acetic anhydride and a drop of sulphuric acid, crystallised from alcohol as fine crystals, m.p. 146-47°. (Found; C, 64.95; H, 6.1. $C_{18}H_{20}O_6$ requires C, 65.1; H, 6.02 per cent).

The *benzoyl* derivative, prepared by benzoyl chloride in presence of pyridine, crystallised from alcohol, m.p. 123°. (Found; C, 69.42; H, 5.5. $C_{23}H_{22}O_6$ requires C, 70.1; H, 5.6 per cent).

The *methoxy* derivative, prepared by dimethyl sulphate in cold, crystallised from dilute alcohol as clusters of needles, m.p. 93-94°. (Found: C, 66.85; H, 6.7. $C_{17}H_{20}O_6$ requires C, 67.1; H, 6.58 per cent).

Hydrolysis of the Ester.—The ester (1g.) was treated with 2N-sodium hydroxide (25 c.c.) for about half an hour on a steam-bath. It was cooled, acidified and the solid crystallised from dilute acetic acid as needles, m.p. 221-22°. (Found: C, 64.4; H, 5.2. $C_{14}H_{14}O_5$ requires C, 64.12; H, 5.34 per cent). The acid is soluble in alcohol and acetic acid, sparingly so in boiling water and insoluble in benzene, chloroform and petroleum ether.

The *acetyl*, *benzoyl* and *anilide* crystallised from alcohol, melting respectively at 209°, 160° and 257°.

Ethyl 7-Hydroxy-6-propyl-4-methylcoumarin-3-acetate.—4-Propyl-resorcinol was prepared by the Clemmensen reduction of resorpiophenone (Chakravarti and Chakravarty, *J. Indian Chem. Soc.*, 1939, **16**, 148).

The resorcinol (2 g.), mixed with ethyl acetosuccinate (3 g.), was treated with concentrated sulphuric acid (10 c.c.) with cooling. It was then worked up as before. The solid was washed with dilute sodium bicarbonate solution and then with water. It was crystallised from alcohol as thin rectangular plates, m.p. 169-70°, yield 1.5 g.

The condensation was studied with phosphorus oxychloride (2 c.c.) as condensing agent and worked up as before. The product was crystallised from rectified spirit as clusters of needles, m.p. 170°, yield about 4 g. (Found: C, 67.9; H, 7.0. $C_{17}H_{20}O_6$ requires C, 67.1; H, 6.6 per cent).

The *acetyl* derivative crystallised from alcohol as needles, m.p. 100°-101°. (Found: C, 65.7; H, 6.1. $C_{18}H_{22}O_6$ requires C, 65.9; H, 6.36 per cent).

The *benzoyl* derivative crystallised from alcohol as rhombic crystals, m.p. 115-16°. (Found: C, 70.2; H, 5.4. $C_{24}H_{24}O_6$ requires C, 70.6; H, 5.9 per cent).

The *methoxy* derivative crystallised from alcohol, m.p. 94-95°.

Hydrolysis:—The 6-propylcoumarin-ester was hydrolysed as before; the acid obtained was crystallised from dilute alcohol, m.p. 199-200°. (Found: C, 61.6; H, 6.4. $C_{15}H_{16}O_5$, H_2O requires C, 61.3; H, 6.13 per cent).

The *acetyl* derivative crystallised from alcohol, m.p. 203°.

The *methoxy* derivative (obtained in course of the methylation of the ester due to hydrolysis) crystallised from dilute acetic acid as short needles, m.p. 176°; (Found. C, 66.0; H, 5.9. $C_{18}H_{18}O_6$ requires C, 66.2; H, 6.2 per cent).

Ethyl 7-Hydroxy-6-butyl-4-methylcoumarin-3-acetate.—4-Butylresorcinol was prepared by the Clemmensen reduction of resbutyrophenone.

4-Butyl resorcinol (2 g.), ethyl aceto-succinate (2.5 g.) and phosphorus oxychloride (3 c.c.) were carefully mixed and kept as before. On working up as before, the product was crystallised from alcohol as needles, m.p. 165-66°. (Found: C, 67.7; H, 7.45. $C_{18}H_{22}O_6$ requires C, 67.93; H, 6.92 per cent).

The *acetyl* derivative crystallised from alcohol, m.p. 116-17°. (Found: C, 67.3; H, 7.3. $C_{20}H_{24}O_6$ requires C, 66.7; H, 6.7 per cent).

The *benzoyl* derivative crystallised from alcohol, m.p. 124°. (Found: C, 71.22; H, 6.05. $C_{25}H_{20}O_6$ requires C, 71.1; H, 6.16 per cent).

The *methoxy* derivative crystallised from alcohol, m.p. 88°.

Hydrolysis.—The above ester was hydrolysed as before. The acid crystallised from dilute alcohol as needles, m.p. 205°. (Found: Equiv., 288.5. $C_{16}H_{18}O_6$ requires Equiv., 290).

The *methoxy* derivative, obtained by hydrolysing the methoxy ester obtained above, crystallised from dilute acetic acid, m.p. 160°. (Found: C, 65.8; H, 6.3. $C_{17}H_{20}O_5$, $\frac{1}{2}H_2O$ requires C, 65.2; H, 6.7 per cent).

Ethyl 7-Hydroxy-4:6-dimethylcoumarin-3-acetate.—4-Methylresorcinol, m.p. 105°, was prepared by the Clemmensen reduction of β -resorcyaldehyde. It is interesting to note in this connection that different specimens of 4-methylresorcinol obtained by different workers are reported to melt at various temperatures ranging from 83-105°. (cf. Clemmensen, *Ber.*, 1914, 47, 51).

4-Methylresorcinol (0.5 g.) was condensed in presence of phosphorus oxychloride (1 c.c.) as before. The product was crystallised from dilute alcohol, m.p. 183-84°. (Found: C, 65.1; H, 5.9. $C_{18}H_{18}O_6$ requires C, 65.2; H, 5.8 per cent).

The *acetyl* derivative crystallised from alcohol as needles, m.p. 168-169°. (Found: C, 64.1; H, 5.7. $C_{17}H_{18}O_6$ requires C, 64.15; H, 5.66 per cent).

Ethyl 7:8-Dihydroxy-6-ethyl-4-methylcoumarin-3-acetate.—4-Ethylpyrogallol was prepared by the Clemmensen reduction of gallacetophenone ("Organic Synthesis", XIV, 40). 4-Ethyl pyrogallol (3 g.), the ester (4.5 g.) and phosphorus oxychloride (3 c.c.) were mixed with cooling in ice. The solid obtained after treatment with water was washed with little acetic acid to remove coloured impurities. The colourless solid obtained was first crystallised from acetone-ligroin mixture and then from benzene as soft silky needles, m.p. 150-51°; yield 3 g. (Found: C, 62.5; H, 5.7. $C_{18}H_{18}O_6$ requires C, 62.74; H, 5.9 per cent). The coumarin dissolves in concentrated sulphuric acid with orange colour and in sodium hydroxide with lemon-yellow colour. It gives green colour with ferric chloride.

The *acetyl* derivative crystallised from alcohol, m.p. 149° mixed m.p. with the original substance depressed to 130-32°. (Found: C, 61.4; H, 5.8. $C_{20}H_{22}O_6$ requires C, 61.54; H, 5.64 per cent).

The *benzoyl* derivative crystallised from alcohol, m.p. 163°.

Hydrolysis.—The ester (1 g.) was dissolved in acetic acid (1 c.c.) and concentrated hydrochloric acid (10 c.c.) added and the mixture refluxed on a steam-bath for nearly 3 hours. On cooling the solid obtained was crystallised from alcohol, m.p. 275°. (Found: Equiv., 280.1. $C_{14}H_{14}O_6$ requires Equiv., 278).

The *acetyl* derivative crystallised from alcohol, m.p. 153-54°. (Found: C, 59.6; H, 5.1. $C_{18}H_{18}O_6$ requires C, 59.7; H, 5.0 per cent).

The C-H determinations are micro-analyses by Prof. T. R. Seshadri, to whom we express our thanks.

We thank Dr. M. S. Shah. Our grateful thanks are expressed to Dr. R. C. Shah, F.N.I. for his sympathetic interest.

BEHAVIOUR OF MERCURIC CHLORIDE AND DETERMINATION OF ITS PARACHOR.

BY W. V. BHAGWAT AND P. M. TOSNIWAL.

Although the solubility of mercuric chloride in organic solvents and its low conductivity at ordinary temperatures are in favour of co-valent nature of mercuric chloride, yet the fact that mercuric chloride is an inorganic metallic salt and that it has abnormally high temperature coefficient of conductivity and that it has coagulating power like other electrolytes confirm its electrovalent character. From results of boiling point measurement mercuric chloride is believed to form aggregates and that its ionisation may be of a higher order. The results of parachor and Raman-effect do not contradict either views.

The abnormal behaviour of mercuric chloride is well known. Although it is purely an inorganic compound, it is more soluble in certain organic solvents.

Mercuric chloride is a metallic chloride and as such is expected to show a high conductivity in aqueous solution. Faraday (*Phil. Trans.*, 1834, 124, 77; 1838, 128, 83) first established the very low conductivity of mercuric chloride both in solid and molten states. A complete reference to the conductivity work may be found in a paper by Joshi and Solanki (*J. Indian Chem. Soc.*, 1940, 17, 627).

In view of this interesting behaviour of mercuric chloride we have tried to see whether determination of parachor throws any light on its constitution. The experimental procedure is the same as in our previous paper (*J. Indian Chem. Soc.*, 1942, 19, 149). Our results are recorded below.

γ = surface tension of the solution. P_m = parachor of the mixture. P_x = parachor of the solute. x = molar fraction of the solute. $1-x$ = molar fraction of the solvent. d = density of the mixture.

TABLE I.

Parachor in ethyl alcohol.

Parachor of absolute alcohol = 124.9.

| x | Temp. | d . | γ . | P_m | P_x . | x | Temp. | d . | γ | P_m . | P_x . |
|---------|-------|--------|------------|-------|---------|---------|-------|--------|----------|---------|---------|
| 0.01592 | 30° | 0.8352 | 20.82 | 126.1 | 201.0 | 0.02051 | 30° | 0.8640 | 21.94 | 126.9 | 219.4 |
| | 50 | 0.8166 | 18.62 | 126.2 | 207.8 | 0.02546 | 40 | 0.8732 | 19.20 | 126.9 | 208.1 |
| | 70 | 0.7962 | 16.78 | 126.1 | 201.0 | 0.02783 | 30 | 0.8822 | 21.41 | 127.6 | 203.9 |

TABLE II.

Parachor in methyl alcohol.

Parachor of methyl alcohol = 88.98.

| Temp. | d . | γ . | P_m | P_x . |
|-------|--------|------------|-------|---------|
| 35° | 0.8608 | 24.67 | 90.90 | 236.5 |
| 45 | 0.8507 | 23.96 | 91.21 | 259.6 |
| 60 | 0.8328 | 21.89 | 91.20 | 239.6 |

TABLE III.

Parachor in ethyl acetate.

| Parachor of ethyl acetate = 213.0. | | | | | | | | | |
|------------------------------------|--------|------------|---------|---------|----------------|--------|------------|---------|---------|
| $x = 0.0320$ | | | | | $x = 0.03558$ | | | | |
| Temp. | d. | γ . | P_m . | P_x . | Temp. | d. | γ . | P_m . | P_x . |
| 30° | 0.9581 | 22.77 | 214.0 | 243.9 | 30° | 0.9729 | 22.78 | 212.2 | 191.1 |
| 40 | 0.9491 | 21.82 | 213.7 | 234.4 | 40 | 0.9607 | 21.98 | 213.0 | 213.6 |
| 60 | 0.9198 | 19.08 | 213.3 | 221.9 | 50 | 0.9449 | 20.67 | 213.3 | 222.0 |
| 65 | 0.9103 | 18.14 | 212.9 | 209.4 | $x = 0.2755$. | | | | |
| $x = 0.03992$. | | | | | 30° | 0.9523 | 22.45 | 212.7 | 203.2 |
| 30° | 0.9811 | 22.76 | 212.2 | 193.0 | 50 | 0.9266 | 20.22 | 212.9 | 210.5 |
| 40 | 0.9690 | 21.94 | 212.9 | 210.4 | 60 | 0.9111 | 18.87 | 212.8 | 206.9 |

TABLE IV.

Parachor in acetone.

| Parachor of acetone = 159.6 | | | | | | | | | |
|-----------------------------|--------|------------|---------|---------|-----------------|--------|------------|---------|---------|
| $x = 0.02327$ | | | | | $x = 0.04345$. | | | | |
| Temp. | d. | γ . | P_m . | P_x . | Temp. | d. | γ . | P_m . | P_x . |
| 15° | 0.8666 | 23.61 | 160.2 | 210.2 | 15° | 0.9317 | 24.71 | 161.0 | 186.3 |
| 20 | 0.8632 | 23.09 | 159.9 | 163.3 | 20 | 0.9274 | 24.23 | 160.9 | 184.1 |
| | | | | | 25 | 0.9243 | 23.69 | 160.6 | 177.1 |

TABLE V.

Parachor in pyridine.

| Parachor of pyridine = 198.2. | | | | | | | | | |
|-------------------------------|-------|------------|---------|---------|-------|-------|------------|---------|---------|
| $x = 0.02328$ | | | | | | | | | |
| Temp. | d. | γ . | P_m . | P_x . | Temp. | d. | γ . | P_m . | P_x . |
| 30° | 1.039 | 36.34 | 197.2 | 154.6 | 50° | 1.019 | 33.83 | 197.6 | 171.8 |
| 40 | 1.030 | 35.34 | 197.5 | 167.6 | 60 | 1.008 | 32.60 | 197.8 | 180.4 |

It is interesting to note that pyridine and mercuric chloride form co-ordination compounds of the type $\text{HgCl}_2 \cdot 2 \text{Py}$, $\text{HgCl}_2 \cdot 4 \text{Py}$ etc.

TABLE VI.

Parachor in distilled water.

Parachor of distilled water = 52.29.

| $x = 0.004844$. | | | | | $x = 0.004199$. | | | | |
|------------------|-------|------------|---------|---------|------------------|-------|------------|---------|---------|
| Temp. | d. | γ . | P_x . | P_m . | Temp. | d. | γ . | P_x . | P_m . |
| 25° | 1.054 | 71.11 | 52.93 | 187.8 | 25° | 1.045 | 69.95 | 52.77 | 169.5 |
| 35 | 1.050 | 70.13 | 53.00 | 202.3 | 45 | 1.036 | 67.72 | 52.79 | 173.3 |
| 45 | 1.046 | 69.01 | 52.98 | 198.1 | 55 | 1.033 | 67.01 | 52.82 | 189.9 |
| 55 | 1.041 | 67.54 | 52.90 | 181.7 | 75 | 1.021 | 66.49 | 52.91 | 202.4 |
| 75 | 1.030 | 64.85 | 52.93 | 187.8 | | | | | |

The calculated value of parachor of mercuric chloride is about 180.

Our view (*J. Indian Chem. Soc.*, 1942, 19, 225) that when atomic and ionic parachors are the same no idea can be formed as regards amount of ionisation seems to be confirmed from these observations. Ray's work (*ibid.* 1938, 15, 43) suggests smaller values for ionic parachors. Hence our results indicate low ionisation which supports conductivity results. Our boiling point results, which are given below indicate higher ionisation at boiling point and thus confirm the high temperature coefficient of conductivity for mercuric chloride.

Jone's work (*Carnegie Inst. Washington*, 1907, p. 60) rules out solvation of mercuric chloride. The high molecular weight of mercuric chloride in organic solvent suggests a tendency to complex formation. It is natural therefore to infer that in water also mercuric chloride forms complex aggregates with higher order of ionisation as suggested by Joshi and Solanki (*loc. cit.*).

TABLE VII.

Molecular weight of mercuric chloride.

| In H ₂ O | | In Et acetate. | | In Et OH | | In MeOH | | In pyridine. | | In acetone | |
|--------------------------|-------|---------------------------|-------|---------------------------|-------|--------------------------|-------|---------------------------|-------|---------------------------|-------|
| Solvent=24.95 g | | Solvent=22.2 | | Solvent=19.46 g | | Solvent=19.79 | | Solvent=24.28 g | | Solvent=19.42 g. | |
| $K_{\text{solvent}}=520$ | | $K_{\text{solvent}}=2790$ | | $K_{\text{solvent}}=1150$ | | $K_{\text{solvent}}=880$ | | $K_{\text{solvent}}=2710$ | | $K_{\text{solvent}}=1670$ | |
| HgCl ₂ | M.W | HgCl ₂ | M.W | HgCl ₂ | M.W | HgCl ₂ | M.W | HgCl ₂ | M.W | HgCl ₂ | M.W |
| 2.4920 g. | 225.7 | 1.925 g. | 302.4 | 2.8984 g. | 305.9 | 5.1680 g. | 302.4 | 2.5062 g. | 329.1 | 4.6576 g. | 336.7 |
| 4.6010 | 245.9 | 3.5216 | 294.9 | 4.7896 | 298.0 | 7.0574 | 285.2 | 4.5376 | 304.1 | 6.2784 | 323.3 |
| 6.2778 | 247.4 | 5.6718 | 295.7 | 7.2894 | 293.0 | 8.3374 | 278.7 | 6.4316 | 296.2 | 8.2386 | 314.9 |
| 8.0554 | 258.3 | 6.9076 | 289.5 | | | | | | | | |

We have studied the coagulating power of mercuric chloride. The sols employed were those of arsenic sulphide, antimony sulphide and manganese dioxide. In arsenic sulphide the order of coagulating power is $\text{Al} > \text{Hg} > \text{Ba} > \text{K}$. In antimony sulphide the order is the same. However in manganese dioxide sol the order is $\text{Ba} > \text{Al} > \text{Hg}$. These abnormal results are in accordance with the results obtained by Ganguly and Dhar (*J. Phys. Chem.*, 1922, 26, 70, 836), Dhar, Sen and Ghosh (*ibid.*, 1924, 28, 457), Chakravarty and Dhar (*ibid.*, 1927, 31, 997), Chatterji and Dhar (*Kolloid Z.*, 1923, 38, 18). The high coagulating power of mercuric chloride supports its electrovalent nature.

Mercuric chloride shows Raman line but this does not contradict its electrovalent nature (*cf.* West and Arthur, *J. Chem. Phys.*, 1934, 2, 215). Moreover Fajan's rule requires mercuric chloride to be electrovalent.

Our thanks are due to Dr. S. S. Joshi of Benares Hindu University for suggesting this problem.

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Received September 17, 1942.

SYNTHESIS OF 2:4-DIMETHOXY- AND 2:4-DIHYDROXY-ISO-PHTHALIC ACIDS.

BY (MISS) K. S. RADHA AND R. C. SHAH.

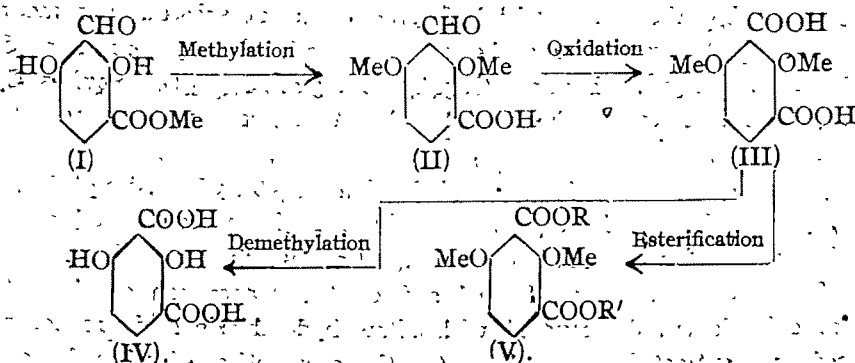
The hitherto unknown 2:4-dihydroxyisophthalic acid and the corresponding 2:4-dimethoxyisophthalic acid have been synthesised by the oxidation of 2:4-dimethoxy-3-formylbenzoic acid, prepared by Shah and Laiwalla's modified Gattermann reaction, with alkaline potassium permanganate. The dimethoxy acid has been esterified and demethylated to the corresponding 2:4-dihydroxyisophthalic acid.

Although 4:6-dimethoxyisophthalic acid and the corresponding dihydroxy acid has been known for a long time (Eijkman, Bergema, Henrard, *Chem. Zentr.*, 1905 I, 816) the isomeric 2:4-dihydroxyisophthalic acid and its dimethyl ether are hitherto unknown. The structure of 2:4-dihydroxyisophthalic acid was assigned to the product of carboxylation of β - or γ -resorcylic acids by heating them with ammonium carbonate and water in a sealed tube (Senhofer, Brunner, *Sitzungsber. A. Akad. Wiss. Wien*, 80, II, 504, 506). However, Späth, Klager and Schloseer (*Ber.*, 1932, 64, 2206) proved that this so-called 2:4-dihydroxyisophthalic acid was really the 4:6-dihydroxyisophthalic acid, identical with that prepared by Eijkman *et al* (*loc. cit.*).

Späth obtained 2:4-dimethoxyisophthalic acid as an oxidation product of osthol (Späth and Pesta, *Ber.*, 1934, 67, 853). He did not isolate the acid but he characterised it as the anilide which was prepared through the acid chloride. The obvious difficulty in the synthesis of such an acid is the introduction of COOH group in the 2' or γ -position. The introduction of CHO group in the 2' or γ -position had already been achieved by Shah and Laiwalla (*J. Chem. Soc.*, 1938, 1828). 2:4-Dimethoxy- and 2:4-dihydroxyisophthalic acids have been synthesised from the aldehyde.

Methyl 2:4-dihydroxy-3-formylbenzoate (I) is prepared by the modified Gattermann reaction (Shah and Laiwalla, *loc. cit.*) on methyl β -resorcyate. The dimethoxy derivative of the corresponding acid (II) is obtained by the methylation of the formyl ester. The dimethoxy acid is then oxidised with alkaline potassium permanganate to 2:4-dimethoxyisophthalic acid (III). This is then demethylated to 2:4-dihydroxyisophthalic acid (IV) by refluxing it with anhydrous aluminium chloride in benzene solution.

The dimethoxy acid on esterification with methyl alcohol and sulphuric acid affords a mixture of the mono and the dimethyl ester, viz., methyl 2:4-dimethoxy-3-carboxybenzoate (V, R=H and R'=Me) or 2:4-dimethoxy-3-carbomethoxybenzoic acid (V, R=Me and R'=H), and methyl 2:4-dimethoxyisophthalate (V, R=R'=Me). The monomethyl ester is assumed to have the structure of methyl γ -2:4-dimethoxy-3-carboxybenzoate (V, R=H and R'=Me), as there is very little possibility of the carboxyl group in the 2' position of being esterified due to steric hindrance.



EXPERIMENTAL

Methyl 2:4-dihydroxy-3-formylbenzoate (I) was prepared by the modified Gattermann reaction on methyl β -resorcyate according to Shah and Laiwalla (*loc. cit.*) and was subsequently methylated to 2:4-dimethoxy-3-formylbenzoic acid (II) also according to the same authors.

Oxidation of 2:4-Dimethoxy-3-formylbenzoic Acid to 2:4-Dimethoxyisophthalic Acid (III).

—The oxidation of the formyl acid was attempted in different ways under different conditions with different quantities of potassium permanganate and using different solvents, and the following method was found to be the best.

2:4-Dimethoxy-3-formylbenzoic acid (5 g.) was dissolved in sodium hydroxide solution (50 c.c., 10%). Potassium permanganate (25 g.) was then added to the alkaline solution in small quantities at a time during about an hour, the mixture being cooled at intervals whenever necessary. At this stage, the solution turned pink, when sodium bisulphite (4 g.) was added to it to reduce the excess of potassium permanganate when the solution acquired a greenish tint. The manganese dioxide was filtered, the solution acidified with hydrochloric acid, concentrated and extracted with ether after salting. On the evaporation of ether a white solid was left which was dissolved in sodium bicarbonate solution (5%), acidified with hydrochloric acid and the salted solution again extracted with ether. A white solid, m.p. 218–20°, was obtained which crystallised from benzene in small shining micro-crystals, m.p. 222–23°, yield 0.6 g. (Found: C, 53.1, H, 4.3. $C_{11}H_{10}O_6$ requires C, 53.1; H, 4.4 per cent).

The precipitated manganese dioxide on boiling with sodium hydroxide (5%) and acidifying the alkaline filtrate with hydrochloric acid and subsequent extraction with ether, yielded some more quantity of the acid, total yield 0.8 g.

The acid gave effervescence with sodium bicarbonate solution and did not react with 2:4-dinitrophenylhydrazine. It was very soluble in methyl and ethyl alcohols, acetone, and fairly soluble in hot water, from which it was crystallised in long needles, m.p. 220–21°.

Methyl 2:4-Dimethoxy-3-carboxybenzoate (V, R=H, and R'=Me) or *2:4-Dimethoxy-3-carbomethoxybenzoic acid* (V, R=Me; R'=H) and *Methyl 2:4-dimethoxyisophthalate*. (V, R=R'=Me).

2:4-Dimethoxyisophthalic acid (0.4 g.) was dissolved in methyl alcohol (12 c.c.). Concentrated sulphuric acid (1.2 c.c., d, 1.84) was then slowly added to the solution and the mixture refluxed on a water-bath for 4 hours. At the end of the reaction, the reaction mixture was poured on to cold water, the solution salted and extracted with ether. The oily product obtained on the evaporation of the ether was treated with sodium bicarbonate solution (5%) and filtered. The insoluble portion, which was the dimethyl ester of the acid, crystallised in colourless long needles from hot water, m.p. 78–80°. (Found: C, 56.4; H, 5.3. $C_{12}H_{14}O_6$ requires C, 56.7; H, 5.5 per cent).

The sodium bicarbonate-soluble portion, which was the monomethyl ester of the acid, was recovered by acidifying the filtrate with hydrochloric acid and subsequent extraction with ether. The solid, obtained on the evaporation of the ether, crystallised in tiny pinkish needles from hot dilute alcohol, m.p. 150–51°. (Found: C, 54.4; H, 5.2. $C_{11}H_{12}O_6$ requires C, 55.0, H, 5.0 per cent). It gives effervescence with sodium bicarbonate solution and gives no colouration with alcoholic ferric chloride.

Demethylation of 2:4-Dimethoxyisophthalic Acid 2:4-Dihydroxy-isophthalic acid (IV).—

2:4-Dimethoxy-iso-phthalic acid (0.3 g.) was dissolved in petroleum ether and anhydrous aluminium chloride (1 g.) was added to the solution which was refluxed on a water-bath for 2 hours. The solution was then filtered and on the evaporation of the petroleum ether the aluminium chloride was decomposed with dilute hydrochloric acid (20 c.c., 1:1) and the solution salted and extracted with ether. On the evaporation of ether the colourless solid obtained was crystallised from hot water in tiny pinkish needles, m.p. 179–81°. (Found: C, 48.2; H, 3.2. $C_8H_6O_6$ requires C, 48.5; H, 3.0 per cent). It gives effervescence with sodium bicarbonate solution and a red colouration with alcoholic ferric chloride.

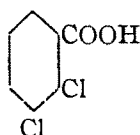
The preparation of the mono and the dimethyl esters of 2:4-dihydroxyisophthalic acid is being attempted.

CHLORINATION OF BENZOIC ACID.

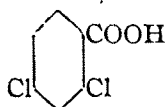
BY H. G. BISWAS AND S. J. DAS-GUPTA.

When benzoic acid is chlorinated with hydrochloric acid and potassium chlorate two isomeric chloro-benzoic acids are obtained. These acids have been found to be 3 : 4-dichloro- and 2 : 5-dichlorobenzoic acids.

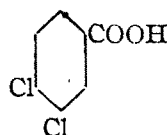
It was shown by three contemporary workers (Pfeifer, *Ber.*, 1871, 6, 658; *ibid.*, 1872, 6, 715; Beilstein, *Annalen*, 1875, 179, 291; Claus, *Ber.*, 1872, 6, 721) that benzoic acid on chlorination by potassium chlorate and hydrochloric acid gives two isomeric dichlorobenzoic acids. The methods adopted by these authors are practically the same. One part of benzoic acid was refluxed with 60 parts of 20% hydrochloric acid to which were slowly added 3 parts of potassium chlorate in concentrated solution. On evaporation of the reaction mixture, the two isomeric dichlorobenzoic acids were obtained as solid crystalline mass. The two acids were separated by fractional crystallisation of the total barium salts from water. The acid which was obtained from less soluble barium salt was called α -dichlorobenzoic acid and that obtained from more soluble barium salt was called β -dichlorobenzoic acid. These authors did not assign any position of the chlorine atoms in the two acids. Afterwards, Seelig (*Annalen*, 1886, 237, 129) in a review of dichloro toluenes and dichlorobenzoic acids described the α -acid as 2 : 3-dichlorobenzoic acid (I) and β -acid as 2 : 4-dichlorobenzoic acid (II).



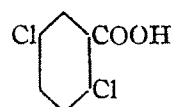
(I)



(II)



(III)



(IV)

It has been conclusively proved by the present authors that the α -dichloro— and β -dichlorobenzoic acids obtained by chlorination of benzoic acid by potassium chlorate and hydrochloric acid by Pfeifer, Beilstein and Claus are 3 : 4- and 2 : 5-dichlorobenzoic acids respectively (III and IV).

The α -dichlorobenzoic acid has been found identical by mixed melting point with an authentic specimen of 3 : 4-dichlorobenzoic acid synthesised from 3 : 4-diaminotoluene by Sandmeyer's reaction and subsequent oxidation. The β -acid has similarly been identified with 2 : 5-dichlorobenzoic acid obtained from 2 : 5-diaminotoluene.

EXPERIMENTAL.

Chlorination of Benzoic Acid.—1200 C.c. of hydrochloric acid (20%) and 20 g. benzoic acid were heated in a flask on wiregauze and a concentrated aqueous solution of 60 g. potassium chlorate was added slowly within a course of 3 to 4 hours. Heating was then continued for several days. On evaporating off the reaction mixture on steam-bath a crystalline mass of a mixture of two dichlorobenzoic acids was obtained.

The crystalline mass was converted into barium salts by heating for 1 hour with excess of barium carbonate in about 200 c.c. of water. It was filtered while hot and the filtrate on cooling yielded crude barium salt of α -dichlorobenzoic acid. The mother liquor was evaporated on steam-bath to a small bulk and cooled when crude barium salt of β -dichlorobenzoic acid was obtained.

The crude barium salt of α -dichlorobenzoic acid was crystallised from water and decomposed

by dilute hydrochloric acid by warming. After cooling and filtering, α -dichlorobenzoic acid was obtained. This was purified by repeated crystallisation from benzene and was finally obtained as colourless needles, m.p. 208.9° . (Found: Cl, 36.92. Calc. for $C_7H_4O_2Cl_2$: Cl, 37.17 per cent). Mixed melting point of this product with an authentic specimen of 3:4-dichlorobenzoic acid was not depressed. The specimen was obtained in the following way. 3:4-Diaminotoluene after Sandmeyer's reaction with cuprous chloride in the usual way furnished 3:4-dichlorotoluene which was oxidised to 3:4-dichlorobenzoic acid by heating with concentrated nitric acid in a sealed tube.

The crude barium salt of β -dichlorobenzoic acid was crystallised from as little water as possible and was similarly decomposed as in the previous case. The β -dichlorobenzoic acid which was obtained was purified by repeated crystallisation from water, and was finally obtained as colourless needles, m.p. 154° . (Found: Cl, 36.89. Calc. for $C_7H_4O_2Cl_2$: Cl 37.17 per cent). Mixed melting point of this product with an authentic specimen of 2:5-dichlorobenzoic acid was not depressed. The specimen of 2:5-dichlorobenzoic acid was obtained from 2:5-diaminotoluene by Sandmeyer's reaction and subsequent oxidation.

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OXIDATION OF RESORCINOL BY HYDROGEN PEROXIDE IN PRESENCE OF TUNGSTIC ACID SOL AS CATALYST.

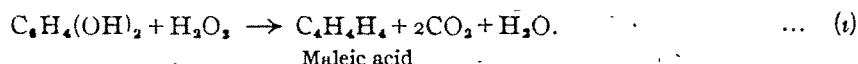
By B. C. KAR.

Oxidation of resorcinol by means of hydrogen peroxide in presence of tungstic acid sol has been carried out. The nature of the end-products and also the kinetics of the reaction have been studied.

The author in his previous publications (*J. Indian Chem. Soc.*, 1938 **15**, 291) has carried out the oxidation of some of the phenols by means of hydrogen peroxide in presence of tungstic acid and molybdic acid sols. In this paper, the oxidation of resorcinol by means of hydrogen peroxide in presence of tungstic acid sol has been described.

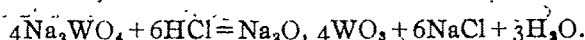
As end-products of the reaction, carbon dioxide and maleic acid have been found out. Carbon dioxide has been estimated quantitatively by absorbing in dry soda-lime. It has been found that 137.3 mg. resorcinol gives 107 mg. carbon dioxide. Maleic acid has been extracted with ether after the reaction is complete.

The mechanism of the reaction as regards the intermediate products and also any other final products are in the course of investigation. The equation may be finally expressed as



Measurement of Kinetics.

Resorcinol of chemically pure grade (Merck) was taken and dissolved in water. In all our experiments we used redistilled water and Schering-Kahlbaum's hydrogen peroxide. The sol was prepared by the addition of hydrochloric acid to sodium tungstate which reacts according to the equation



In order to study the kinetics, the pressure of carbon dioxide developed during the course of the experiment was measured at constant volume using high concentration of hydrogen peroxide. To determine the velocity coefficient the following expression was used

$$k = \frac{1}{t_2 - t_1} \cdot \log \frac{P_\infty - P_{t_1}}{P_\infty - P_{t_2}},$$

where P_{t_1} is the pressure in cm. of mercury at any time t_1 (in minutes) and P_{t_2} is the pressure at time t_2 , P_∞ is the pressure that should develop when the reaction is complete. It may be obtained by means of the equation

$$X = h \frac{V_0 \frac{273}{T} + V_{r,a}}{P_0},$$

where X = the volume of gas evolved in c.mm. at N. T. P. which may be easily obtained from the amount of carbon dioxide formed. The amount of carbon dioxide can be calculated from the equation (i) or experimentally determined by absorbing in soda-lime.

h = corresponding reading of the manometer = P_∞ .

V_0 = the volume of the gas space in the vessel.

T = absolute temperature of the water bath. V = volume of the liquid in the vessel, α = the solubility of carbon dioxide in the liquid of the vessel at N.T.P. = 0.759 (Bohr, *Ann. Phys. Chem.*, 1899, **68**, 504). P_0 = normal pressure = 760 mm. mercury.

The experiments were carried out in a Warburg-Barcroft apparatus. The increase of pressure due to the production of carbon dioxide was indicated by a manometer, filled with mercury. The total volume up to the constant mercury level in the manometer was 48.4 c.c. and was determined by filling the vessel and the tube with mercury. The reaction mixture occupied 10 c.c. No carbon dioxide was formed by the action of hydrogen peroxide on resorcinol in absence of the sol. The whole system was shaken 55 to 60 times per minute throughout the experiment. The vessels were completely immersed in a big thermostat which was maintained at the required temperature. To correct for the changes of temperature and the barometric pressure a similar vessel which contained only water was used. It was always observed by keeping strict control in which the carbon dioxide was absorbed by caustic potash in a suitable reservoir that there was very slight spontaneous decomposition of hydrogen peroxide during the course of the experiment. The experimental results are given below.

TABLE I.

Effect of varying the conc. of resorcinol.
Temp. = 28°. $p_H = 1.18$. $H_2O_2 = 0.72M$
Sodium tungstate = 0.01M.

| | | | |
|----------------|---------|--------|--------|
| Resorcinol (M) | 0.00625 | 0.0125 | 0.025 |
| k (mean) | 0.0015 | 0.0017 | 0.0018 |

TABLE II.

Effect of varying the conc. of H_2O_2
Temp. = 28°. $p_H = 1.18$. Resorcinol = 0.025M.
Sodium tungstate = 0.01M.

| | | | | |
|--------------|--------|--------|--------|--------|
| H_2O_2 (M) | 0.18 | 0.36 | 0.72 | 1.08 |
| k (mean) | 0.0011 | 0.0015 | 0.0018 | 0.0020 |

TABLE III.

Effect of varying the conc. of sodium tungstate.
Temp. = 28°. $p_H = 1.18$. $H_2O_2 = 0.72M$.
Resorcinol = 0.025M.

| | | | | |
|----------------------|--------|--------|--------|--------|
| Sodium tungstate (M) | 0.005 | 0.01 | 0.015 | 0.02 |
| k (mean) | 0.0011 | 0.0018 | 0.0024 | 0.0029 |

TABLE IV.

Effect of varying the p_H .
Temp. = 28°. Resorcinol = 0.025M.
 $H_2O_2 = 0.72M$. Sodium tungstate = 0.01M.

| | | | |
|-------|--------|--------|--------|
| p_H | 1.18 | 2.5 | 4.3 |
| k | 0.0018 | 0.0019 | 0.0017 |

The oxidation can similarly be carried out in presence of molybdic acid sol.

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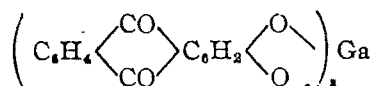
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NEW COMPOUNDS OF GALLIUM. PART V. GALLIUM ALIZARIN LAKES, GALLIUM SALTS OF GEOMETRICALLY AND OPTICALLY ISOMERIC ACIDS AND DOUBLE SULPHATES WITH ETHYLENE- AND PROPYLENEDIAMINE SULPHATES.

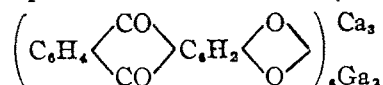
By PANCHANAN NEOGI AND KANAI LAL MONDAL.

Gallium alizarate and gallium-calcium alizarate have been obtained. These 'lakes' are red in colour, the gallium lake being as scarlet as the corresponding aluminium compound and the calcium-gallium lake dull red in colour. These can be fastened on cotton, woolen and silk fabrics. Other salts prepared are *d*- and *l*-gallium camphor sulphonates and their optical rotations have been measured. Ethylene- and propylenediammonium gallium sulphates have also been prepared.

In the present paper more new compounds of gallium are described. Two gallium lakes with alizarin have been prepared. One is gallium alizarate, the other is calcium-gallium alizarate. The gallium lake is obtained as a scarlet precipitate and has the composition $\text{Ga}(\text{C}_{14}\text{H}_7\text{O}_4)_3$ like the corresponding aluminium and trivalent iron and chromium alizarates (Mahlau, *Ber.*, 1913, **46**, 443). It dissolves readily in ammonia and other alkalis and should contain one hydroxyl group. The compound may be represented as



If the solution of gallium alizarate in ammonia is treated with an equivalent quantity of calcium chloride the remaining hydroxylic hydrogen is replaced by the bivalent metal and calcium-gallium alizarate is obtained as a red precipitate. The compound has the composition $\text{Ga}_2\text{Ca}_3(\text{C}_{14}\text{H}_7\text{O}_4)_6$ and may be represented as



This compound is analogous to the corresponding aluminium, iron and chromium lakes containing calcium obtained by Mahlau (*loc. cit.*). The two compounds are stable substances and may be precipitated as red dyes on cotton, woolen and silk fabrics in the same manner as aluminium alizarates are used as a dye, the gallium lake being as scarlet as the aluminium lake. The red dye obtained as calcium-gallium alizarate has a less scarlet shade than the gallium alizarate.

In our attempts to prepare gallium salts of geometrically and optically isomeric acids, it has been possible to prepare a gallium salt of maleic acid by dissolving *freshly prepared* gallium hydroxide in maleic acid but gallium fumarate could not be obtained in a similar manner. Both *d*- and *l*-camphorsulphonic acids also dissolved freshly prepared gallium hydroxide and gave dextro rotatory and laevo rotatory camphorsulphonates respectively. The optical rotations of these compounds have been measured in aqueous solutions. Other compounds described are the double salts of gallium sulphate with ethylenediamine and propylenediamine sulphates.

EXPERIMENTAL.

Gallium Alizarate.—A concentrated aqueous solution of potassium alizarate was prepared. When it was added to an aqueous solution of gallium nitrate or sulphate, a scarlet precipitate of gallium alizarate was at once formed. It was filtered, washed thoroughly with water and then dried in air. [Found: C, 63.24; H, 2.66; Ga, 8.21. $(\text{C}_{14}\text{H}_7\text{O}_4)_3\text{Ga}$ requires C, 64.04; H, 2.7; Ga, 8.89 per cent].

It is insoluble in water but soluble in alcohol. It dissolves readily in ammonia. Gallium alizarate is a fast lake for cotton fibres. The fibre is first dipped into a solution of alizarin in caustic soda or caustic potash and afterwards into an aqueous solution of a gallium salt. The fibre is then dyed deep red which cannot be washed out by soaping. Fibres of wool and silk can also be dyed using gallium alizarate as a lake.

Calcium-gallium Alizarate.—Gallium alizarate (2 g.) was dissolved in ammonia when a violet solution was obtained. Calcium chloride (0.5 g.) was also dissolved in water. The two solutions were then mixed. At once a dull red precipitate appeared. The precipitate was allowed to settle and then filtered. After washing thoroughly with water it was dried in air. [Found: C, 59.03; H, 2.42; Ga, 8.01; Ca, 7.56. $(C_{14}H_6O_4)_6Ga_2Ca_3$ requires C, 59.71; H, 2.13; Ga, 8.29; Ca, 7.11 per cent]. It is insoluble in water and ammonia. Calcium-gallium alizarate is a fast lake for cotton, wool and silk.

Gallium Maleate.—Excess of freshly prepared gallium hydroxide was treated with an aqueous solution of maleic acid when a portion of it dissolved. The undissolved hydroxide was filtered off and the filtrate evaporated in a vacuum desiccator over sulphuric acid. It could also be evaporated on a water-bath. The solid obtained was crystallised from water and analysed after drying in air for two days. [Found: C, 27.85; H, 2.16; Ga, 27.32. $(C_4H_2O_4)_3Ga_2 \cdot 2H_2O$ requires C, 27.8; H, 1.93; Ga, 27.03 per cent]. Gallium maleate is a white crystalline substance. It is soluble in water and is not decomposed by boiling with water for a short time.

Gallium dextroCamphorsulphonate.—It was prepared by dissolving gallium hydroxide in an aqueous solution of *d*-camphorsulphonic acid and evaporating the solution obtained in a vacuum desiccator over sulphuric acid. It was purified by crystallisation from water and analysed after drying between folds of filter papers. [Found: S, 11.24; Ga, 8.23. $(C_{10}H_{15}SO_4)_3Ga \cdot 3H_2O$ require S, 11.75; Ga, 8.57 per cent]. 5% Solution gave $[\alpha]_D^{25} = +18.6$; $[M] = +152$. The camphor-sulphonate is very soluble in water. It is also soluble in alcohol.

Gallium laevoCamphorsulphonate.—It was obtained as a crystalline solid like the dextro compound by using freshly prepared gallium hydroxide and *l*-camphorsulphonic acid. [Found: S, 11.16; Ga, 8.49. $(C_{10}H_{15}SO_4)_3Ga \cdot 3H_2O$ requires S, 11.75; Ga, 8.57 per cent]. It is similar in properties to the *dextro* compound except that it is *laevorotatory* in solution. 5% Aqueous solution gave $[\alpha]_D^{25} = -19$. $[M] = -155$.

Ethylenediammonium Gallium Sulphate.—Saturated aqueous solutions of ethylenediamine sulphate and gallium sulphate taken in equimolecular proportions were mixed. The double sulphate was then precipitated by the addition of alcohol and ether to the mixed solution. It was then crystallised from water and obtained in the form of colourless plates. [Found: N, 3.52; Ga, 17.91; SO_4 , 48.37. $Ga_2(SO_4)_3 \cdot C_2H_4(NH_3)_2SO_4 \cdot 12H_2O$ requires N, 3.49; Ga, 17.46; SO_4 , 47.88. per cent]. It is soluble in water but insoluble in alcohol. On keeping, it did not change and remained completely soluble in water.

Propylenediammonium Gallium Sulphate.—It was obtained as the ethylenediamine compound by mixing together saturated aqueous solutions of a molecule of propylenediamine sulphate and a molecule of gallium sulphate and precipitating by means of alcohol and ether. [Found: N, 3.69; Ga, 17.81; SO_4 , 46.5. $Ga_2(SO_4)_3 \cdot C_3H_7(NH_3)_2SO_4 \cdot 12H_2O$ requires N, 3.43; Ga, 17.16; SO_4 , 47.06 per cent]. In crystalline form and properties it is similar to the corresponding ethylene diammonium compound.

ON THE PHOTOBROMINATION OF CINNAMIC ACID IN ULTRAVIOLET LIGHT OF $254\mu\mu$.

By J. C. GHOSH AND S. K. BHATTACHARYYA.

The kinetics and mechanism of the bromination of cinnamic acid in ultraviolet light of $254\mu\mu$ in solution of carbon tetrachloride have been studied in details. Results which have been found are quite different from those found with visible light by various workers. The reaction is unimolecular with respect to bromine as well as with respect to cinnamic acid. The velocity constant is directly proportional to the intensity of radiation absorbed by cinnamic acid and is independent of the nature of polarisation of light. The temperature coefficient and the quantum efficiency are more than unity. A mechanism involving activated cinnamic acid molecules has been suggested.

The photobromination of cinnamic acid and stilbene has been investigated by various workers, notably by Berthoud and Béranecq (*J. chim. phys.*, 1927, **24**, 213) and by Ghosh and Purakayastha (*J. Indian Chem. Soc.*, 1926, **3**, 261; 1927, **4**, 409; *Z. physikal. Chem.*, 1930, **B**, **9**, 154) in non-polar solvents like CCl_4 , CS_2 , etc. It is generally agreed that in these photobrominations in visible light, bromine atoms are the photoactive agents which start a chain reaction and the velocity is given by the equation,

$$-\frac{d[\text{Br}_2]}{dt} = k_3[\text{Br}_2] \frac{\sqrt{k_1 I}}{k_2} \cdot \frac{k_5[A]}{k_4 + k_5[A]}$$

The object of the present investigation was to find out whether any bromination could be carried out in ultraviolet light of wave-length $254\mu\mu$ which is very slightly absorbed by bromine, but completely absorbed by cinnamic acid in extremely dilute solutions.

Ghosh and Biswas (*Z. Elektrochem.*, 1924, **30**, 97) have investigated the molecular extinction coefficients of cinnamic acid in wave-length $254\mu\mu$ and found it to be about 10,000. Thus in $254\mu\mu$ cinnamic acid is the absorbing substance while bromine acts as an acceptor molecule.

EXPERIMENTAL.

The experimental arrangement was the same as was described by the authors in previous works (*Z. physikal. Chem.*, 1936, **B**, **32**, 145; *J. Indian Chem. Soc.*, 1941, **18**, 257) with a few alterations:—(a) The reaction cell was 1.8 cm. \times 1.8 cm. \times 0.5 cm. thick and made of plane quartz plates fused into one another with a stopper at the top; (b) the spectral region $254\mu\mu$ was isolated with the help of a quartz cylindrical cell containing a strong solution of bromine (0.2M) in CCl_4 placed in front of the window between the lens and the reaction cell.

Merck's extra pure cinnamic acid further purified by crystallisation and Merck's extra pure "reagent" bromine were used throughout. Merck's extra pure CCl_4 further purified by distillation over fused CaCl_2 was used.

Determination of the Velocity of Reaction.—The velocity of the reaction was determined by pipetting out 0.32 c.c. of the reaction mixture and titrating iodometrically with 0.01N-thio-sulphate solution by means of a microburette. The reactions were carried out at 31° and 41° .

The light passing through the bromine filter contains much red light which was found to be not altogether ineffective in bringing about the photochemical bromination of cinnamic acid. To eliminate the effect of red light the following arrangement was made. Two experiments were done for each composition of the reaction mixture. One, with the total light emerging through three quartz cells containing pure water, 0.2M bromine solution in CCl_4 and lastly, pure

carbon tetrachloride placed in series; the other, with the light emerging through three quartz cells in series containing pure water, 0.2M bromine solution in CCl_4 and lastly a strong solution of cinnamic acid in CCl_4 (0.25M). In the first case the velocity of reaction was due to radiation 254 $\mu\mu$ and to red light. In the second case it was due to red light only as the cinnamic acid of 0.25M strength completely absorbed the 254 $\mu\mu$ radiation.

Measurement of Intensity.—The intensity of radiation (254 $\mu\mu$) absorbed by the cinnamic acid solution was measured by means of a Moll galvanometer and Moll thermopile, calibrated by means of a standard lamp supplied by the "Bureau of Standards". The intensity was measured by noting the deflections when the light passed (a) through bromine filter alone, and (b) bromine filter + cinnamic acid filter. The difference in deflections in the two cases gave the intensity of 254 $\mu\mu$ radiation absorbed by the cinnamic acid.

All the experiments in this investigation were finished within one hour of the exposure during which no dark reaction was observed between cinnamic acid and bromine at temperatures between 31° and 41°.

The experimental data are recorded in Tables I to V. The velocity constant in this investigation was calculated according to the simple monomolecular equation, viz.,

$$k_0 = \frac{2.3}{t} \log \frac{a}{a-x}$$

where a is the initial concentration of bromine in g. mols. per litre and x , the change in concentration of bromine in time t minutes. The experimental data did not fit any other equation.

One typical experiment is recorded below.

TABLE I.

$a = 0.102M$. b (initial conc. of cinnamic acid) = 0.05M. I_{abs} (number of quanta absorbed by cinnamic acid per c.c. per sec.) = 19.4×10^{13} . $\lambda = 254\mu\mu$. θ (temp.) = 31°

| t | T_1 | T_2 | T_3 | $k_0 \times 10^4$ | γ |
|-----|-------|-------|-------|-------------------|----------|
| 20 | 0.85 | 0.56 | 0.29 | 22.6 | 11.8 |

T_1 = titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.32 c.c. of the reaction mixture when exposed to light passing through bromine filter for t minutes; T_2 = titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.32 c.c. of the reaction mixture when exposed to light passing through bromine filter and cinnamic acid filter in series in time t minutes; T_3 = titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.32 c.c. of the reaction mixture due to reaction only for 254 $\mu\mu$ in t minutes; and γ = quantum efficiency.

Similar calculations were made in all the experiments and the results are summarised in Tables II to V. In the tables $\theta = 31^\circ$ and $\lambda = 254 \mu\mu$.

TABLE II.

Effect of varying the concentration of bromine.

$I_{\text{abs.}} = 19.4 \times 10^{13}$. $b = 0.05M$

| a | $k_0 \times 10^4$ | γ |
|--------|-------------------|----------|
| 0.102M | 22.6 | 11.8 |
| 0.075 | 22.3 | 8.8 |
| 0.054 | 23.6 | 6.8 |
| 0.037 | 20.6 | 3.6 |
| 0.025 | 20.6 | 2.6 |

TABLE III.

Effect of varying the concentration of cinnamic acid.

$I_{\text{abs.}} = 34.4 \times 10^{13}$. $a = 0.05M$.

| b | $k_0 \times 10^4$ | γ |
|--------|-------------------|----------|
| 0.075M | 60.4 | 7.5 |
| 0.05 | 40.2 | 5.2 |
| 0.0375 | 28.2 | 3.9 |
| 0.025 | 19.2 | 2.6 |

PHOTOBROMINATION OF CINNAMIC ACID IN ULTRAVIOLET LIGHT OF 254 $\mu\mu$ 505

From Table II we see that k_s is independent of the initial concentration of bromine and from Table III, k_s is proportional to the concentration of cinnamic acid.

TABLE IV.

Effect of varying the intensity of radiation absorbed by cinnamic acid.

$a = 0.05M.$

| $I_{abs.} \cdot 10^{-13}$ | b. | $k_s \times 10^4$ |
|---------------------------|--------|-------------------|
| 34.4 | 0.075M | 60.4 |
| 14.1 | " | 24.0 |
| 34.4 | 0.05 | 40.2 |
| 14.1 | " | 16.4 |

TABLE V.

Effect of varying temperature.

$I_{abs.} = 34.4 \times 10^{13}. a = 0.05M.$

| b. | $k_s \times 10^4$ | | v. |
|-------|---------------------|---------------------|-----|
| | $\theta = 31^\circ$ | $\theta = 41^\circ$ | |
| 0.05M | 40.2 | 60.9 | 1.5 |
| 0.025 | 19.2 | 29.0 | 1.5 |

From Table IV we see that k_s is directly proportional to the intensity of radiation absorbed by cinnamic acid. In Table V, v stands for temperature coefficient for 10° rise. From this table we see that the temperature coefficient of the reaction is of the order 1.5.

Reaction in Polarised Light.—The reaction was also carried out in plain polarised, *d*-circularly polarised and *l*-circularly polarised lights but no difference was observed in the behaviour of unpolarised, plane polarised and *d*- and *l*-circularly polarised lights. The velocity constant was found to be independent of the nature of polarisation of light. The description and the working principle of the polarising apparatus have been discussed in details by Ghosh *et al.* (*J. Indian Chem. Soc.*, 1937, **14**, 495).

DISCUSSION.

The reaction has the following characteristics:

(a) The reaction is unimolecular with respect to bromine as well as with respect to cinnamic acid; (b) there is no induction period; (c) the rate of reaction is directly proportional to the intensity of radiation absorbed by cinnamic acid; (d) the temperature coefficient is 1.5; (e) the quantum efficiency is more than unity; (f) the rate of reaction is independent of the nature of polarisation of light.

The peculiar feature of this reaction is that the rate of reaction is directly proportional to the intensity of radiation absorbed by cinnamic acid. Again the quantum efficiency is more than unity which indicates that the reaction is attended with some kind of chain formation. The following simple mechanism explains all the observed facts.

A molecule of cinnamic acid is activated by the absorption of a quantum of radiation of 254 $\mu\mu$. The activated cinnamic acid molecules may be deactivated either spontaneously or by collision with inert solvent molecules or with the walls of the containing vessel but may be stabilised by collision with unactivated cinnamic acid molecules. The dibromocinnamic acid molecules are formed when the activated cinnamic acid molecules collide with bromine molecules.

Thus



where C, C^* and CBr_2 are the molecules of cinnamic acid, activated cinnamic acid and dibromocinnamic acid respectively.

The rate of formation of $C^* = I/E$, where $E = Nh\nu$. The rate of deactivation of C^* is directly proportional to the concentration of C (unactivated cinnamic acid molecules).

Thus the rate of deactivation of $C^* = \frac{k_2[C^*]}{[C]}$

$$[C^*] = \frac{I/E \cdot [C]}{k_2}$$

Hence

$$-\frac{d[Br_2]}{dt} = k_3[C^*][Br_2]$$

$$= k_3 \frac{I/E \cdot [C]}{k_2} \cdot [Br_2]$$

$$= k^1 \cdot I/E \cdot [C][Br_2]. \quad \dots (a)$$

The relation (a) agrees well with the experimental observation recorded in Tables I to IV that the rate of reaction is unimolecular with respect to both cinnamic acid and bromine and also that the rate is proportional to the intensity of radiation absorbed by cinnamic acid.

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PHOTOCHEMICAL OXIDATION OF MANDELIC ACID BY BROMINE WITH TUNGSTIC ACID SOL AS SENSITISER IN ULTRAVIOLET LIGHT OF 254 $\mu\mu$.

By J. C. GHOSH, S. K. BHATTACHARYYA AND K. R. KAR.

A detailed investigation has been made on the oxidation of mandelic acid by bromine with tungstic acid sol as the sensitizer in ultraviolet light of 254 $\mu\mu$. The reaction is unimolecular with respect to bromine and also with respect to mandelic acid. The velocity constant passes through a maximum at $p_H 4.05$ and it is independent of the concentration of sodium tungstate so long as the p_H is constant. The velocity constant is proportional to the intensity of radiation absorbed by tungstic acid sol. Temperature coefficient is small and the quantum efficiency is more than unity. A mechanism has been suggested.

Ghosh and Purakayastha (*Z. physikal. Chem.*, 1932, **B**, 9, 54) have already shown that bromine reacts with mandelic acid directly only at wave-lengths above 313 $\mu\mu$. In the region below 313 $\mu\mu$ the reaction is a purely sensitised one. Ghosh and Roy (*Z. physikal. Chem.*, 1936, **B**, 82, 158) have studied the photochemical oxidation of mandelic acid by bromine in wave-length 254 $\mu\mu$ with uranyl sulphate as sensitizer. The object of the present investigation was to study the same photochemical oxidation with tungstic acid sol as photosensitizer in wave-length of 254 $\mu\mu$.

The oxidation of mandelic acid by bromine in presence of tungstic acid sol occurs in the dark to a small extent. By adding a very dilute solution of potassium bromide (0.005 *M*) to the reaction mixture the dark reaction was completely stopped. Ghosh and Purakayastha (*Z. physikal. Chem.*, 1930, **B**, 7, 285; *J. Indian Chem. Soc.*, 1929, 6, 361) have shown that the photo-oxidation of mandelic acid by bromine is unimolecular in the absence of KBr and also in presence of a small quantity of KBr; and the length of the dark reaction chain following the primary photo-process in this case is quite considerable. In the presence of excess of KBr it is found, however, that the reaction becomes zero molecular and simultaneously the chain length is also considerably diminished. A small addition of KBr at the start ensures the advantage that the bromine ion, produced during the initial stages of the reaction when the velocity is being measured, does not exert any perceptible retarding effect, if it is very much less than the bromine molecules already present. In the present investigation the reaction was found to be unimolecular.

EXPERIMENTAL.

The experimental arrangement was the same as was described by Ghosh and Bhattacharyya in the previous paper (*this issue*, p. 503).

Kahlbaum's extra pure mandelic acid, Merck's extra pure 'reagent' bromine, Merck's pure potassium bromide, sodium tungstate and HCl were used. For making solutions bi-distilled water was used.

The velocity of reaction was found to follow a unimolecular course with respect to bromine, the velocity constant being calculated according to $k = \frac{1}{t} \cdot \log \frac{a}{a-x}$ where a is the initial concn-

tration of bromine in g. mols per litre and x , the change in concentration of bromine in g. mols per litre in time t minutes. The experimental data are recorded in Tables I to VI.

λ =wave-length ; I_{abs} =no. of quanta absorbed by tungstic acid sol per c.c. per second ; θ =temperature ; t =time in minutes ; T_1 =titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.29 c.c. of the reaction mixture when exposed to light passing through bromine filter for t minutes ; T_2 =titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.29 c.c. of the reaction mixture when exposed to light passing through bromine filter and tungstic acid sol filter in series for t minutes ; T_3 =titre difference in c.c. of 0.01N-thiosulphate corresponding to 0.29 c.c. of the reaction mixture due to reaction only for 254 μ in t minutes ; and γ =quantum efficiency.

TABLE I.

$\lambda=254 \mu$. Mandelic acid=0.25 M. Na-tungstate=0.025 M. HCl=0.0383 M.
KBr=0.005 M. $I_{\text{abs}} = 35.4 \times 10^{-12}$. $\theta=30^\circ$. $p_H=4.05$.

| Conc. of total Br ₂ . | t . | T_1 . | T_2 . | T_3 . | $k \times 10^{-4}$. | γ . |
|----------------------------------|-------|---------|---------|---------|----------------------|------------|
| 0.044 M | 200 | 0.82 | 0.55 | 0.27 | 5.6 | 6.4 |
| 0.028 | 200 | 0.62 | 0.45 | 0.17 | 5.5 | 4.3 |
| 0.02 | 200 | 0.40 | 0.28 | 0.12 | 5.5 | 3.1 |

Effect of varying the Concentration of Bromine.

From Table I we see that the velocity constant is independent of the initial concentration of bromine.

TABLE II.

$I_{\text{abs}} = 1.8 \times 10^{-12}$.

Total Br₂=0.028M.

Other conditions same as in Table I.

Mandelic acid.

| Mandelic acid. | $k \times 10^{-4}$. | γ . |
|----------------|----------------------|------------|
| 0.25 M | 1.4 | 4.5 |
| 0.31 | 1.7 | 5.3 |
| 0.38 | 2.2 | 6.9 |
| 0.45 | 2.5 | 7.7 |

TABLE III.

Total Br₂=

0.003M.

Other conditions same as in Table I.

p_H . $k \times 10^{-4}$.

| p_H . | $k \times 10^{-4}$. | γ . |
|---------|----------------------|------------|
| 5.52 | 1.6 | 1.5 |
| 5.4 | 2.0 | |
| 4.05 | 5.7 | |
| 2.66 | 0.9 | |
| 2.12 | 0.8 | |

TABLE IV.

Mandelic acid=0.31M.

Total Br₂=0.032.

Other conditions same as in Table I.

Tungstate. $k \times 10^{-4}$.

| Tungstate. | $k \times 10^{-4}$. |
|------------|----------------------|
| 0.125 M | 2.2 |
| 0.025 | 2.3 |
| 0.0375 | 2.2 |

TABLE V.

Total Br₂=0.032M.

Other conditions

same as

in Table I.

$I_{\text{abs}} \times 10^{-12}$ Mandelic acid.

| $I_{\text{abs}} \times 10^{-12}$ | Mandelic acid. | $k \times 10^{-4}$. |
|----------------------------------|----------------|----------------------|
| 11.2 | 0.31 M | 2.3 |
| 22.1 | " | 4.3 |
| 11.2 | 0.42 | 3.0 |
| 22.1 | " | 5.6 |

From Table II, we see that the velocity constant is proportional to the concentration of mandelic acid.

Effect of varying the p_H of the Solution.—The velocity constant passes through a maximum at $p_H = 4.05$.

Effect of varying the Concentration of Sodium Tungstate.—From Table IV we see that the velocity constant is independent of the concentration of sodium tungstate so long as the p_H is kept constant.

Effect of varying the Intensity.—It is evident from TABLE V that the velocity constant is directly proportional to the intensity of radiation absorbed by tungstic acid sol.

TABLE VI.

Effect of varying the temperature.

$\lambda = 254 \mu\mu$. $I_{abs} = 8.8 \times 10^{12}$. $p_H = 4.05$. v = Temperature coefficient for 10° rise. Total $Br_2 = 0.032 M$.

| Mandelic acid. | Tungstate. | HCl | Total Br_2 . | KBr. | $k \times 10^{-4}$ | | v |
|----------------|------------|----------|----------------|---------|---------------------|---------------------|------|
| | | | | | $\theta = 30^\circ$ | $\theta = 40^\circ$ | |
| 0.31 M | 0.025 M | 0.0383 M | 0.032 M | 0.005 M | 1.7 | 2.3 | 1.35 |

DISCUSSION.

The reaction has the following characteristics :—

(a) The velocity of reaction is unimolecular with respect to bromine and also with respect to mandelic acid; (b) there is no induction period; (c) the velocity constant is independent of the concentration of sodium tungstate so long as the hydrogen-ion concentration is kept constant; (d) the velocity constant passes through a maximum at $p_H 4.05$; (e) the temperature coefficient is small; (f) the velocity constant is proportional to the intensity of radiation absorbed by tungstic acid sol; (g) the quantum efficiency lies between 1 and 7.

The fact that the velocity constant is proportional to the intensity of absorbed radiation and not to its square root leads to the conclusion that bromine atoms are not the active reagents. The simplest mechanism of reaction may be imagined as follows.

The surface concentrations of both bromine and mandelic acid on tungstic acid micelle are proportional to their respective bulk concentrations. A centre of reaction on the tungstic acid micelles produced by absorption of a quantum of radiation is reduced by a neighbouring mandelic acid molecule. The reduced tungstic acid is in its turn oxidised by a molecule of bromine. When the stationary state is reached, the velocity of oxidation of mandelic acid is equal to the velocity of reduction of bromine and each in its turn is proportional to the respective surface concentration. The observation that one quantum of radiation can transform several molecules can only be explained on the basis that the energy-rich product of reaction may bring into activation new centres of reaction on the surface of the tungstic acid micelles.

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STUDIES ON PHOTOCHEMICAL REACTIONS BETWEEN AMMONIUM MOLYBDATE AND VARIOUS ORGANIC REDUCING AGENTS IN WAVE-LENGTH 366 $\mu\mu$.

BY S. K. BHATTACHARYYA, K. R. KAR AND A. R. SUR.

The reduction of ammonium molybdate by tartaric acid, mandelic acid and lactic acid in ultraviolet light of 366 $\mu\mu$ has been studied. The products of photoreduction vary in their physicochemical properties. Depending on the relative concentrations of the molybdate and the reductant, the reaction products are sometimes green, sometimes greenish yellow, sometimes pale yellow and even colourless. The green product predominates in excess concentration of molybdate and the colourless product predominates in excess concentration of the reductant. The kinetics of the reaction vary when the end-products of reaction are different. It has been found that the maximum velocity of reaction is obtained when the end-product is pale yellow in colour, the velocity of transformation being always less when the green products are formed.

Ghosh and his collaborators (*J. Indian Chem. Soc.*, 1936, **14**, 495) have made quantitative investigations on the oxidation of various reducing agents by photoactive sols of tungstic acid, molybdic acid, uranic acid, vanadic acid and ceric borate in both polarised and unpolarised lights. The results obtained may be grouped into two heads:—(i) with tungstic, vanadic and ceric borate sols, *l*-circularly polarised light has been found to be more effective than *d*-circularly polarised light in bringing out the photochemical reaction; (ii) with molybdic and uranic acid sols, *d*- and *l*-circularly polarised lights have been found to have the same efficiency.

Hakomori (*Sci. Rep. Tohoku*, 1927, **16**, 841) has shown that hexavalent uranium salt in neutral solution forms a complex with tartaric acid in molecular proportions and this complex undergoes photochemical reduction to the quadrivalent state on exposure to sunlight. Dumansky and Diatschkovsky (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1053) have shown that sodium tungstate forms a colloidal complex with tartaric acid solution which becomes blue on exposure to light. Gernez (*Compt. rend.*, 1887, **104**, 785; **105**, 85; 1889, **108**, 942) investigated the changes in rotatory power of solutions of tartaric acid in presence of alkali molybdates with increasing concentration. He found maximum rotations when the acid and salts were mixed in equimolar proportion and this fact was considered to point to the formation of definite complex salts. The same method was adopted by Rosenheim and Itzig (*Ber.*, 1900, **33**, 707) with tartaric acid and alkali molybdates and polymolybdates and also with tungstates and polytungstates. Klason and Kohler (*Ber.*, 1901, **34**, 3946) extended Itzig's work and found that the maximum rotations given by sodium hydrogen tartrate depend on other factors beside the amount of alkali metal, such as the ratio of molybdic acid, concentration of the active substance and the temperature of the solution. Compounds of the general formula $R_2(XO_3)_2 \cdot C_4H_4O_6$ (R =alkali metal; X =Mo, W) have been prepared by Rosenheim and Itzig in the crystalline form. That complex formation occurs when ammonium molybdate is mixed with weak organic acids, *viz.*, tartaric acid, lactic acid and mandelic acid, is supported by Britton and Jackson (*J. Chem. Soc.*, 1934, 1055).

The object of the present investigation was to study in details, the photoreduction of the complexes formed of ammonium molybdate and the various organic reducing acids, *e.g.*, tartaric acid, mandelic acid and lactic acid in both polarised and unpolarised light.

EXPERIMENTAL.

The experimental arrangement was the same as was described by Ghosh and Bhattacharyya in a previous paper (*this issue*, p. 503) with one alteration. The spectral region of 366 $\mu\mu$ was isolated with the help of "Schott and Gen ultraviolet filter no. 312".

Reagents.—Merck's extra pure ammonium molybdate, and *d*-tartaric acid, *l*-tartaric acid and racemic acid supplied by "Dr. Landau and Frankel Co." further purified by crystallisation; Kahlbaum's extra pure *l*-lactic acid and *r*-mandelic acid were used throughout the investigation. For making solutions bi-distilled water was used. For p_H control Merck's extra pure HCl was used.

Measurement of the Velocity of Reaction.—The velocity of reaction was determined by pipetting out 0.98 c.c. of the reaction mixture in a conical flask containing 5 c.c. of dilute H_2SO_4 (1:20) and titrating the reduced molybdate with 0.0115N- $KMnO_4$ solution by means of a microburette. It is to be pointed out here that $KMnO_4$ solution of the above concentration cannot oxidise tartaric acid, lactic acid or mandelic acid in the cold; so that the reduced molybdate was easily estimated by means of 0.0115N- $KMnO_4$ in presence of the above reducing acids. The reactions were carried out at 29°. The p_H value of the mixture was measured electrometrically by using a quinhydrone electrode.

The reduction of ammonium molybdate by tartaric acid, lactic acid and mandelic acid does not proceed in the dark but on exposure to light of radiation 366 μ rapid reaction goes on.

The products of photoreduction vary in their properties. Depending on the relative concentrations of the molybdate and the reductant, the reaction products are sometimes green, sometimes greenish yellow, sometimes pale yellow and even colourless. The green product predominates in excess of molybdate, and the colourless product predominates in excess of the reductant. The kinetics of photochemical reactions will naturally vary when the end-products of reaction are different. We have found that the maximum velocity of photochemical reaction is obtained when the end-product is pale yellow in colour, the velocity of transformation being always less when the green products are formed.

Intensity Measurement.—The intensity of radiation absorbed by the reaction mixture was measured by means of a Moll galvanometer and a Moll thermopile calibrated by means of a standard lamp, supplied by the Bureau of Standards. The intensity of absorbed radiation was measured by noting the deflections when the light passed through (a) pure water alone and (b) the reaction mixture. The difference in deflections in the two cases gave the intensity of radiation absorbed by the reaction mixture.

The results are tabulated in Tables I to VIII. In the given tables $\Delta x/\Delta t$ =zero molecular velocity constant=changes in concentration of 0.98 c.c. of ammonium molybdate per minute in terms of c.c. of 0.0115N- $KMnO_4$.

TABLE I.

Effect of varying the concentrations of both ammonium molybdate and tartaric acid.

Reductant=d-tartaric acid. Temp. (θ)=29°. p_H = 1.71. Wave-length (λ)=366 μ .

| Conc. of Mo.* | Concentration of tartaric acid in normality. | | | | | | | | | |
|---------------|--|--------|-------|-----------------|-------------|------------|-----------------|-------------|-------------|------------|
| | | 0.025. | 0.05. | 0.075. | 0.1. | 0.125. | 0.2. | 0.4. | 0.6. | 0.8. |
| 0.025N | $\Delta x/\Delta t.10^4$ | ... | 20.0 | 30.8 | 30.2 | 20.4 | 13.7 | ... | 10.8 | ... |
| | Colour of the product | ... | Green | Pale yellow | Colourless | Colourless | Colourless | ... | Colourless | ... |
| | $I_{abs}.10^{-13}$ | ... | 41.0 | 41.0 | 41.0 | 41.0 | 41.0 | ... | 53.8 | ... |
| 0.05 | $\Delta x/\Delta t.10^4$ | ... | ... | 30.0 | 30.0 | 30.3 | ... | 20.1 | 20.0 | ... |
| | Colour | ... | Green | Greenish yellow | Pale yellow | ... | Colourless | Colourless | ... | ... |
| | $I_{abs}.10^{-13}$ | ... | ... | 42.8 | 44.0 | 44.2 | ... | 50.0 | 53.8 | ... |
| 0.1 | $\Delta x/\Delta t.10^4$ | ... | 10.0 | 21.6 | 30.0 | 43.3 | 43.3 | 43.3 | 43.3 | 43.3 |
| | Colour | ... | Green | Green | Green | Green | Greenish yellow | Pale yellow | Colourless | Colourless |
| | $I_{abs}.10^{-13}$ | ... | 53.8 | 57.0 | 57.0 | 57.0 | 57.0 | 57.0 | 57.0 | 57.0 |
| 0.2 | $\Delta x/\Delta t.10^4$ | ... | 5.5 | 9.09 | 16.6 | 21.6 | 27.0 | 43.0 | 86.6 | 86.6 |
| | Colour | ... | Green | Green | Green | Green | Green | Green | Pale yellow | Colourless |
| | $I_{abs}.10^{-13}$ | ... | 54.4 | 54.4 | 54.4 | 54.4 | 54.4 | 55.6 | 55.6 | 55.6 |

I_{abs} =no. of quanta absorbed per c.c. per second.

* The equivalent weight of molybdate has been calculated on the basis of one equivalent containing one gram atom of molybdenum.

TABLE II.

Effect of varying the concentration of both ammonium molybdate and mandelic acid.

Reductant = *r*-Mandelic Acid. $\theta = 29^\circ$. $p_H = 1.71$. $\lambda = 366 \mu\mu$.

| Conc. of Mo. | | Conc. of 0.025 | 0.05 | 0.1 | 0.2 | 0.3 | 0.4 |
|--------------|----------------------------------|-------------------|-------------|-----------------|-----------------|-----------------|-------------|
| 0.025N | $\Delta x / \Delta t \cdot 10^4$ | 16.6 | 40.0 | 34.4 | 34.7 | 36.6 | — |
| | Colour | Green | Pale yellow | Colourless | Colourless | Colourless | — |
| | $I_{abs} \cdot 10^{-13}$ | 65.4 | 65.4 | 65.4 | 69.2 | 69.8 | — |
| 0.05 | $\Delta x / \Delta t \cdot 10^4$ | 14.2 | 25.0 | 43.3 | 53.3 | 80.0 | — |
| | Colour | Green | Green | Greenish yellow | Pale yellow | Colourless | — |
| | $I_{abs} \cdot 10^{-13}$ | 65.4 | 76.2 | 76.2 | 76.2 | 76.2 | — |
| 0.1 | $\Delta x / \Delta t \cdot 10^4$ | 10.4 | 21.7 | 40.0 | 80.0 | 120.0 | 123.3 |
| | Colour | Green | Green | Green | Greenish yellow | Pale yellow | Colourless |
| | $I_{abs} \cdot 10^{-13}$ | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 |
| 0.2 | $\Delta x / \Delta t \cdot 10^4$ | 8.8 | 16.6 | 33.0 | 67.0 | 120.0 | 123.3 |
| | Colour | Green | Green | Green | Green | Greenish yellow | Pale yellow |
| | $I_{abs} \cdot 10^{-13}$ | 72.0 | 74.0 | 74.0 | 74.0 | 74.0 | 74.0 |

TABLE III.

Effect of varying the conc. of *l*-lactic acid. $\theta = 29^\circ$. $p_H = 1.71$. $\lambda = 366 \mu\mu$. Conc. of Mo = 0.2 N.

| Conc. in normality of lactic acid. | 0.15 | 0.2 | 0.3 | 0.4 | 0.6 | 0.8 |
|------------------------------------|-------|-------|-------|-----------------|-------------|------------|
| $\Delta x / \Delta t \cdot 10^4$ | 14.1 | 25.0 | 37.0 | 53.3 | 65.2 | 63.1 |
| Colour | Green | Green | Green | Greenish yellow | Pale yellow | Colourless |
| $I_{abs} \cdot 10^{-13}$ | 55.8 | 60.0 | 60.0 | 60.0 | 60.0 | 60.0 |

TABLE V.

Effect of varying the intensity of absorbed radiation.

 $\lambda = 366 \mu\mu$. $\theta = 29^\circ$. $p_H = 1.71$.

| $I_{abs} \cdot 10^{-13}$ | Mo. | Reductant. | $\Delta x / \Delta t \cdot 10^4$ | $(\Delta x / \Delta t)_I$ $(\Delta x / \Delta t)_H$ | $[I_{abs}]_I$ $[I_{abs}]_H$ |
|--------------------------|------|------------|----------------------------------|--|--------------------------------|
| <i>d</i> -Tartaric acid. | | | | | |
| I | 57.0 | 0.1N | 0.1N | 43.3 | 4.6 |
| II | 10.0 | 0.1 | 0.1 | 9.3 | 5.7 |
| <i>r</i> -Mandelic acid. | | | | | |
| I | 74.0 | 0.2 | 0.2 | 67.0 | 3.9 |
| II | 19.2 | 0.2 | 0.2 | 17.1 | 3.9 |
| <i>l</i> -Lactic acid. | | | | | |
| I | 60.0 | 0.2 | 0.2 | 25.0 | 4.9 |
| II | 11.6 | 0.2 | 0.2 | 5.2 | 5.2 |

TABLE VII.

Effect of varying the p_H . $\theta = 29^\circ$. $\lambda = 366 \mu\mu$. Conc. of Mo = 0.2 N.

| $I_{abs} \cdot 10^{-13}$ | p_H | [Tartaric acid]. | $\Delta x / \Delta t \times 10^4$ |
|--------------------------|-------|------------------|-----------------------------------|
| 54.4 | 4.95 | 0.025N | 4.6 |
| 54.4 | 1.71 | " | 5.5 |
| 54.4 | 4.09 | 0.075 | 12.1 |
| 54.4 | 1.71 | " | 16.6 |

TABLE IV.

Effect of varying the conc. of ammonium molybdate.

 $\theta = 29^\circ$. $p_H = 1.71$. $\lambda = 366 \mu\mu$. Lactic acid = 0.4 N.

| Conc. of Mo in normality. | 0.0125 | 0.025 | 0.05 | 0.1 | 0.2 |
|----------------------------------|------------|------------|------------|------------|-----------------|
| $\Delta x / \Delta t \cdot 10^4$ | 7.0 | 14.7 | 26.3 | 53.1 | 53.3 |
| Colour | Colourless | Colourless | Colourless | Colourless | Greenish yellow |
| $I_{abs} \cdot 10^{-13}$ | 52.0 | 56.0 | 56.0 | 60.0 | 60.0 |

TABLE VI.

Effect of varying the nature of tartaric acid.

 $I_{abs} \times 10^{-13} = 57.0$. λ , and p_H as in Table V.

| | Conc. of Mo. | Conc. of Reductant. | $\Delta x / \Delta t \cdot 10^4$ |
|-------------------------|--------------|---------------------|----------------------------------|
| <i>d</i> -Tartaric acid | 0.1N | 0.1N | 43.3 |
| <i>l</i> -Tartaric acid | " | " | " |
| Racemic acid. | " | " | " |

TABLE VIII.

Quantum efficiency of the process.

 $\lambda = 366 \mu\mu$. $\theta = 29^\circ$. $p_H = 1.71$. n = No. of molecules transformed per c.c. per second.

| Conc. of Mo. | Conc. of reductant. | $n \cdot 10^{-13}$ | $I_{abs} \cdot 10^{-13}$ | γ |
|--------------------------|---------------------|--------------------|--------------------------|----------|
| <i>d</i> -Tartaric acid. | | | | |
| 0.2N | 0.2N | 50.9 | 55.6 | 0.9 |
| 0.1 | 0.1 | 51.3 | 57.0 | 0.9 |
| 0.2 | 0.4 | 102.7 | 55.6 | 1.8 |
| <i>r</i> -Mandelic acid. | | | | |
| 0.2 | 0.2 | 20.2 | 19.2 | 1.1 |
| 0.1 | 0.1 | 47.4 | 72.4 | 0.7 |
| 0.2 | 0.3 | 142.2 | 74.3 | 1.9 |
| <i>l</i> -Lactic acid. | | | | |
| 0.2 | 0.2 | 29.6 | 59.9 | 0.5 |
| 0.2 | 0.6 | 77.2 | 61.0 | 1.3 |

Thus we see that the velocity constant increases slightly with decrease in p_H .

From Table V, we see that the velocity of reaction is directly proportional to the intensity of absorbed radiation. From Table VI we see that different optical isomeric tartaric acids as well as racemic acid have got the same efficiency in the photoreduction of ammonium molybdate. Table VIII shows that quantum efficiency is nearly unity.

It was found that unpolarised, plane polarised, *d*- and *l*- circularly polarised lights are equally effective in bringing out photoreduction of ammonium molybdate by *d*-tartaric acid, *l*-tartaric acid, racemic acid, *l*-lactic acid and α -mandelic acid.

DISCUSSION.

Table I.—(a) With excess of tartaric acid, the products are always colourless and the whole of the incident radiation is absorbed. In the vertical column corresponding to 0.4*N* tartaric acid, it will be seen that the velocity of reaction increases as the concentration of molybdate increases; the proportionality is nearly exact.

(b) For relatively low concentration of tartaric acid, when the reaction product is definitely green, horizontal columns 3 and 4 show that for a fixed concentration of molybdate the velocity of reaction is also proportional to the concentration of tartaric acid. Again comparison of the data in horizontal column 3 with the corresponding data in horizontal column 4 show that for the same amount of light absorption, the velocity is inversely as the concentration of molybdate.

(c) The velocity of reaction for any one concentration of molybdate becomes maximum when the relative concentration of molybdate and tartrate are such that the reaction product looks pale yellow in colour. In this region the reaction mixture consists approximately of two equivalents of tartaric acid to one equivalent of molybdate, the equivalent weight of molybdate being calculated on the basis of one equivalent containing one gram atom of molybdenum.

Table II.—The results with mandelic acid as reductant are generally similar to those obtained with tartaric acid as reductant. Thus, for excess concentration of mandelic acid, 0.3*N*, when the reaction products are colourless $[Mo] = 0.025N, 0.05N$, the velocity of reaction is approximately proportional to the concentration of molybdate. Again, as will be seen from horizontal columns 2, 3 and 4, when the reaction products are definitely green-coloured, for any one concentration of molybdate, the velocity of reaction is proportional to the concentration of mandelic acid. In this region also the reaction velocity for any one concentration of mandelic acid diminishes as the concentration of molybdate increases. The pale yellow solutions, which are obtained by reduction, in the region of concentration 1 Mo:2 mandelic acid (approximately), are characterised by the maximum velocity of reaction.

Tables III and IV.—The experimental data on the velocity of photoreduction of molybdate by lactic acid are similar in general features to those observed with tartaric acid or mandelic acid as reductant.

The authors wish to express their thanks to Dr. J. C. Ghosh for the facilities he has given us in carrying out this work.

THE REDUCTION OF AMMONIUM MOLYBDATE BY *l*-SODIUM HYDROGEN ASCORBATE IN THE DARK.

BY S. K. BHATTACHARYYA AND A. R. SUR.

The reduction of ammonium molybdate by *l*-sodium hydrogen ascorbate has been studied in the dark. It has been found that when the concentration of sodium hydrogen ascorbate and ammonium molybdate are equivalent, the velocity of reaction is a maximum. For excess concentrations of either reagent, the velocity is less. This indicates that the velocity of reaction is proportional to the concentration of the complex formed by the association of an equivalent of ascorbate with one equivalent of molybdate.

Ascorbic acid, since its isolation in the pure state, has been a material of absorbing interest. During the past few years a large amount of work has been done on the physiological action as well as on the various physicochemical properties of ascorbic acid. Herbert and co-workers (*J. Chem. Soc.*, 1933, 1270) made for the first time a careful investigation of some of the physicochemical properties of ascorbic acid obtained from nature. Ghosh and Rakshit (*Biochem. Z.*, 1936, 289, 15; 1937, 289, 395; 1938, 297, 153) and Ghosh (*J. Indian Chem. Soc.*, 1938, 16, 1) made a detailed investigation of the physicochemical properties of synthetic *l*-ascorbic acid and dehydro-ascorbic acid. The present investigation was carried out to study in details, reduction of ammonium molybdate with sodium hydrogen ascorbate.

It was found that just on mixing the ascorbate with ammonium molybdate a yellow colour is developed which with time becomes green due to reduction of the molybdate. The yellow colour of the mixture is due to the formation of a complex.

EXPERIMENTAL.

The reaction cell ($4 \times 4 \times 0.5$ cm.) made of plane glass plates fused into one another with a stopper at the top was placed inside a double jacketed metal box. The temperature was kept constant by passing, with the aid of a circulating pump, water from a thermostat through the annular space of the box.

Reagents.—*l*-Light's extra pure synthetic *l*-ascorbic acid; Merck's extra pure ammonium molybdate and NaOH and resublimed iodine were used. For making solutions redistilled water was used.

Since ascorbic acid or an ascorbate is easily oxidised by air in presence of moisture, fresh solutions of ascorbic acid was prepared every time just before each experiment. Sodium hydrogen ascorbate was prepared every time by adding an equivalent of NaOH to ascorbic acid solution. It is known that p_H value of sodium hydrogen ascorbate is near about 6. The p_H value of ammonium molybdate was determined electrometrically using a quinhydrone electrode and adjusted to 6. On mixing sodium hydrogen ascorbate to ammonium molybdate the p_H will remain nearly constant.

Since it is very difficult to determine accurately the p_H of ascorbic acid or an ascorbate the principle of isohydry was adopted in keeping the p_H constant.

Determination of the Velocity of Reaction.—The velocity of reaction was determined by pipetting out 0.36 c.c. of the reaction mixture in a conical flask containing 5 c.c. of *N*-HCl and then estimating the ascorbic acid with 0.0112 *N*-iodine solution by means of a microburette. It is to be noted here that iodine cannot oxidise the reduced molybdate formed. The experimental data are recorded in Table I. The reaction has been studied only up to 10-15% conversion. In Table I, $\Delta x / \Delta t \cdot 10^4$ has been tabulated where $\Delta x / \Delta t$ represents the change in concentration of

0.36 c.c. of ascorbic acid per minute in terms of c.c. of 0.0112N-iodine. [Mo]=concentration of ammonium molybdate in g. equivalents per litre, the equivalent weight of molybdate being calculated on the basis of one equivalent containing one g. atom of molybdenum.

TABLE I.

Effect of varying the concentrations of both ammonium molybdate and sodium hydrogen ascorbate.

$p_H=6.0$. Temp. = 29° .

| Conc. of sodium hydrogen ascorbate in normality. | | | | |
|--|-------|-------|-----------------|---|
| 0.0125 | 0.025 | 0.05 | 0.1 | |
| Conc. of Mo = 0.05N. | | | | |
| $\Delta x / \Delta t \times 10^4$ | 5.5 | 9.8 | 7.7 | 4.5 |
| Colour | Green | Green | Greenish yellow | Yellow (original colour) of the completed |
| Conc. of Mo = 0.05N. | | | | |
| $\Delta x / \Delta t \times 10^4$ | 3.3 | 14.4 | 39.0 | 20.9 |
| Colour | Green | Green | Green | Greenish yellow |
| Conc. of Mo = 0.1N. | | | | |
| $\Delta x / \Delta t \times 10^4$ | 2.21 | 12.2 | 40.0 | 145.0 |
| Colour | Green | Green | Green | Green |

DISCUSSION.

It is remarkable that when the concentrations of sodium hydrogen ascorbate and ammonium molybdate are equivalent the velocity of reaction is maximum. This indicates that the velocity of reaction is proportional to the concentration of the complex formed by the association of one equivalent of ascorbate with one of molybdate. For excess concentrations of either reagent the velocity diminishes which goes to show that the complex is stabilised by both molybdate and ascorbate. This conclusion is further supported by the fact that for equivalent concentrations

$$\frac{dx}{dt} = k [\text{complex}] = k' (A - x) (B - x)$$

where A and B represent conc. of molybdate and ascorbate and x = complex formed.

If x is small compared with A or B , and when $A = B$,

$$\left[\frac{dx}{dt} \right]_1 = k' A^2, \quad \left[\frac{dx}{dt} \right]_2 = k' A^2,$$

From Table I we see that for 0.025N concentrations of both ascorbate and molybdate,

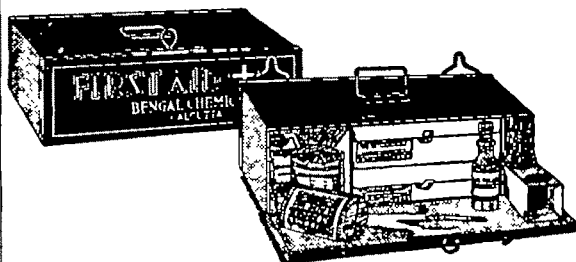
$$\frac{dx}{dt} = 9.8 \times 10^{-4}$$

and for 0.05N concentrations of both molybdate and ascorbate $dx/dt = 39.0 \times 10^{-4}$ and for 0.1N concentrations of both molybdate and ascorbate, $dx/dt = 145.0 \times 10^{-4}$. These results support the mechanism suggested.

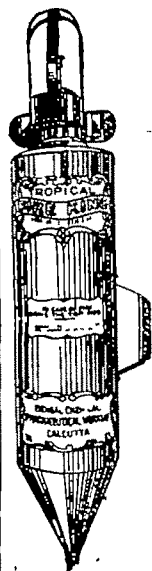
The authors wish to express their thanks to Dr. J. C. Ghosh for his kind help and advice.

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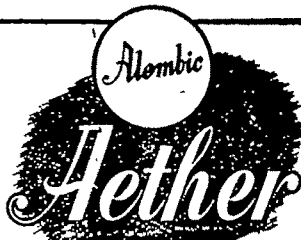
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